

As noted above, the slag sample collected for testing had a relatively high carbon content (31.6% carbon or 68.4% ash), which may be due to the fact that the facility was undergoing commissioning and testing when it was collected. Our assumption that the slag generated during normal operations would have a lower carbon content was borne out by subsequent reports from plant personnel. Therefore, in the design of the facility, it was assumed that the slag feed would contain a maximum of 17% unconverted carbon or char by weight. This would generate ~276 tons/day of slag under post-commissioning steady-state operations. Assuming that the slag/char separation facility would be operated for one shift per day at ~90% availability, its required throughput capacity would be 40 tons/hour.

The installed capital cost for a char separation facility using ground storage (Steps 1-3) was estimated at \$307,000. The direct operating costs for the facility were estimated at \$0.84/ton of slag feed, which includes operating and maintenance labor, and maintenance materials.

2.5.3 TEC Clean Slag Production Economics

The economics of producing a char-free, saleable slag were developed and compared with slag disposal costs. Typically, the disposal costs for such materials is in the \$6-\$10/ton range. The slag processing costs, in the range of \$0.84/ton, are considerably lower than the disposal alternative. Commercially available aggregate prices in the vicinity of the gasifier are in the \$5-\$8/ton range. The facility would generate product slag at 70-80% recovery on a feed basis. This analysis is presented in Table 40.

Table 40. Slag Char Separation Costs and Economics Summary

Item	Design Basis
Plant Design Data & Assumptions	
<i>Coal used</i>	2,300 tons/day
Ash in coal (10%)	230 tons/day
Slag generated	276 tons/day
Slag processing facility operating schedule	8 hours/day
Slag processing average feed	34.5 tons/hour
<i>Facility design basis</i>	40.0 tons/hour
<i>Gasifier operation</i>	300 days/year
Raw slag feed generated/year	82,800 tons/year
Slag saleable product, 70-80% of feed	70%
Saleable slag produced/year	57,960 tons/year
Facility Capital & Direct Operating Costs*	
<i>Capital costs for the facility</i>	\$307,000
Direct operating costs per year	\$69,648/year
Operating costs per ton	\$0.84/ton
Economics	
<i>Slag sale price</i>	\$5/ton
Revenues generated from slag sale	\$289,800/year
Net revenues after deducting operating costs	\$220,152/year
Payback period	1.4 years

*All figures are given in 1998 dollars.

As may be seen in the table, there is a net minimum margin of \$4.16/ton, and the facility would generate net revenues of \$220,000 per year, with a payback period of less than two years. It was therefore concluded that separation of char from slag to make a saleable slag product is economically viable.

2.5.4 Conduct Applications-Oriented Testing of TEC Slag

In view of the interest at TEC in using this technology, tests were conducted to identify and confirm the potential for utilizing the char-free slag in four applications. The results are summarized below.

Cement Concrete Aggregate: Tests were conducted to determine whether a 2,000-psi concrete could be made from the char-free slag using a mix comprising 5-6 sacks of concrete per cubic yard as is typically used in the production of masonry products (blocks, bricks, stepping stones, etc.), concrete grout, mortar mix, and ready mix, etc. These tests were performed at the laboratory scale using a mix design that had been developed for previous testing. Two-inch cubes were made to obtain 7-day and 28-day compressive strength values. The test results are given in Table 41. The results indicate that the TEC slag can be used as an aggregate to produce precast products and for concrete mixes requiring 2000 to 4000 psi strength.

Table 41. Utilization of Char-Free TEC Slag as Aggregate in Cement Concrete

Weight % Aggregates			Cement, Sacks/Yd ³	Compressive Strength, psi	
Coarse Aggregate	Slag	Total		7-Day	28-Day
50	50	100	6	3975	4287
25	75	100	6	3170	3487
0	100	100	6	3479	3895

Road Construction and Maintenance. The char-free TEC slag was compared with similar slags for its suitability for utilization as a road construction aggregate, and was also checked against the duty requirements for the above application. The particle size and other general properties of the TEC slag are similar to those of most other slags. Therefore, it is considered to be suitable for road construction and maintenance applications such as sub-base and base material and seal coat aggregate.

Industrial Material (Roofing Granule, Industrial Filler, Abrasive Grit). A sieve analysis comparison of the char-free TEC slag indicated that it can be used as an industrial material for a variety of applications.

Lightweight Aggregate Production. Muffle furnace tests were performed to determine the suitability of the char-free TEC slag for making lightweight aggregates, based on the procedure used for many other slags previously. The results, given in Table 42, were positive. However, additional work is needed for the production of ultra-lightweight aggregates, which are below 12 lb/ft³ unit weight.

Table 42. Utilization of TEC Slag as Feedstock for LWA Production

Test No.	Feed	1	2	3	4	5
Temp. °F	Ambient	1450	1500	1600	1700	1800
Unit Wt, lb/ft ³	109.0	94.2	88.9	80.0	64.0	55.0

2.5.5 Utilization of Slag/Char Separation Process at DOE-Funded IGCC Plants

Under this subtask, Praxis tested a slag sample obtained from the Wabash River Repowering Project IGCC plant to study its expansion characteristics. This slag was added to the test program with the objectives of extending the project findings to another slag, exploring the potential for removal of the char from the slag, and producing a high-strength expanded product with a unit weight in the 50-55 lb/ft³ range which would meet the requirements for structural concrete applications. The results of the tests were presented to a management team representing the Wabash River Repowering Project, consisting of Destec (Dynergy), and PSI, at the gasification site. It was concluded that while specific process operating parameters may vary depending on the individual slag, the technology developed by Praxis for slag/char separation and the

production of lightweight aggregates could be applied at the commercial scale to all the gasification slags tested.

2.5.6 Conclusions

A sample of the slag from the TEC IGCC plant, which is currently disposed of as a solid waste, was obtained for testing. The sample contained 31.3% carbon (68.7% ash). Based on our testing and analysis, we arrived at the following conclusions:

- Tests with the TEC slag confirmed the results obtained for other slags that a saleable char-free slag product can be generated at the commercial scale. Application of Praxis' slag/char separation process resulted in two fractions:
 - A 63.9% slag fraction containing 5% carbon (the maximum acceptable limit for carbon in slag set by TEC)
 - A 46.3% saleable (0% carbon or 100% ash) slag product.

Higher recovery is achievable with slag samples obtained more recently.

- Weight percent recovery of char-free slag is a function of the carbon content of the as-generated slag. For the TEC sample, 70-80% recovery of char-free slag is possible.
- The study confirmed that the char-free TEC slag could be used in numerous commercial applications including as an aggregate in cement concrete. Tests also confirmed that it could be used in high-value applications such as feedstock for production of lightweight aggregates which sell for \$40/ton.
- Commercial-scale separation of slag and char can be accomplished by retrofitting the slag/char process modules as needed at the TEC IGCC plant. The Praxis process is especially applicable at this site (both in terms of the individual steps and as a total package) due to the high carbon content of the slag at this site.
- Both capital costs of the Praxis slag/char separation process at \$207,000 and operating costs at \$0.84/ton are low.

2.6 Laboratory Studies of Slag as Raw Material in Portland Cement Kiln Feed (Task 2.6)

The objectives of using coal gasification slag as a raw material in making Portland cement are threefold: (i) as a partial replacement for conventional raw materials, (ii) to explore the potential for using slag as a fluxing agent to reduce the firing temperature thus lowering kiln energy requirements, and (iii) to decrease the kiln retention time thus increasing the kiln capacity. Initially, bench-scale tests were conducted at Pennsylvania State University using a conventional high-temperature furnace. Although a high-temperature furnace is not quite comparable to the rotary kiln normally used for making cement clinker, its use as an initial test for the clinkering capability of the gasifier slag is appropriate. In the formation of cement clinker, the most

important process is the liquid state sintering of the raw materials under high temperature in a kiln (usually of the rotary type). Therefore, the ability of slag to form a clinker is very important.

Basic mix designs for testing were developed based on the formulation of a conventional Type I portland cement. Several different levels of slag were tested, with the maximum dictated by the overall chemistry of the mix. A baseline portland cement kiln feed material was procured from a cement plant in Pennsylvania with the help of Fuller Co. and shipped to Pennsylvania State University for laboratory tests. A slag sample used previously for other tasks on this project was used in the laboratory testing after grinding to -200 mesh. The temperature and retention time of the raw material were monitored. In order to ascertain the effects of slag addition, tests were performed to establish baseline data and to thoroughly characterize the cement clinker raw feed and clinkers made at different temperatures. These tests include x-ray diffraction analysis, isothermal calorimetry, and TGA thermal analysis.

Composition of Portland Cement and Cement Nomenclatures. The terminology pertaining to common portland cement is used in these sections on the use of slag as a portland cement kiln feed material. Portland cement clinker is produced by burning a mixture of limestone and clay or shale in a high-temperature rotary kiln. The resultant clinker contains a mixture of distinct oxide compounds. It is customary to report chemical analyses as contents of oxides since the compounds have empirical formulae given by the addition of the oxide formula. Although such relationships are useful for calculation of quantities they tell us nothing about the structural nature of the compounds. The typical chemical composition of portland cement clinker is as follows:

Oxides	%
SiO ₂	21.7
Al ₂ O ₃	5.3
Fe ₂ O ₃	2.6
CaO	67.7
MgO	1.3
K ₂ O	0.5
Na ₂ O	0.2
SO ₃	0.7
Free lime	1.5

The compounds, on the other hand, are usually a mixture of these oxides. Therefore, a special shorthand notation is used to simplify formulas. As in refractories technology, single letters replace the usual oxides formula, as shown below.

Oxide:	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	H ₂ O	Na ₂ O	Na ₂ O	SO ₃
Symbol:	C	S	A	F	H	N	K	S

For example, the most abundant compound in portland cement clinker is tricalcium silicate (3CaO-SiO₂), which in shorthand notation is: C₃S.

Typically, portland cement clinker consists of the following major compounds:

Compounds	%
C ₃ S	65.4
C ₂ S	12.9
C ₃ A	9.6
C ₄ AF	7.9

Laboratory Studies. Prior to usage, the pre-blended baseline portland cement kiln feed material was subjected to x-ray diffraction analysis. The result is shown in Figure 2. TGA thermal analysis over the range of 122-1922°F (50-1050°C) of this material is shown in Figure 3. The x-ray diffraction pattern of the raw feed shows a typical portland cement kiln feed with diffraction peaks dominated by calcium carbonate (limestone). The TGA weight loss trace was used to examine the weight loss characteristics of the raw feed with temperature. As can be seen clearly in the thermal trace, the majority of the weight loss occurs in the ~1382-1607°F (750-875°C) temperature range, which corresponds to the liberation of CO₂ from the calcium carbonate. This information was used to design a heating curve for the clinkering process in order to allow sufficient time for the CO₂ to be released. A batch of the raw feed was then clinkered in a high-temperature molybdenum furnace at various temperatures using a platinum crucible. The temperature profile used was:

- Ramp to 1652°F (900°C) in 4 hours
- 1652°F (900°C) calcine for 4 hours
- 1652°F (900°C) to *clinkering temperature* in 2 hours
- Sinter at *clinkering temperature* for 4 hours
- Air quench to ambient temperature

The clinkering temperatures used for this study were 2012°F (1100°C), 2192°F (1200°C), 2372°F (1300°C), and 2642°F (1450°C). Normal clinkering temperature in a cement kiln is about 2642°F (1450°C).

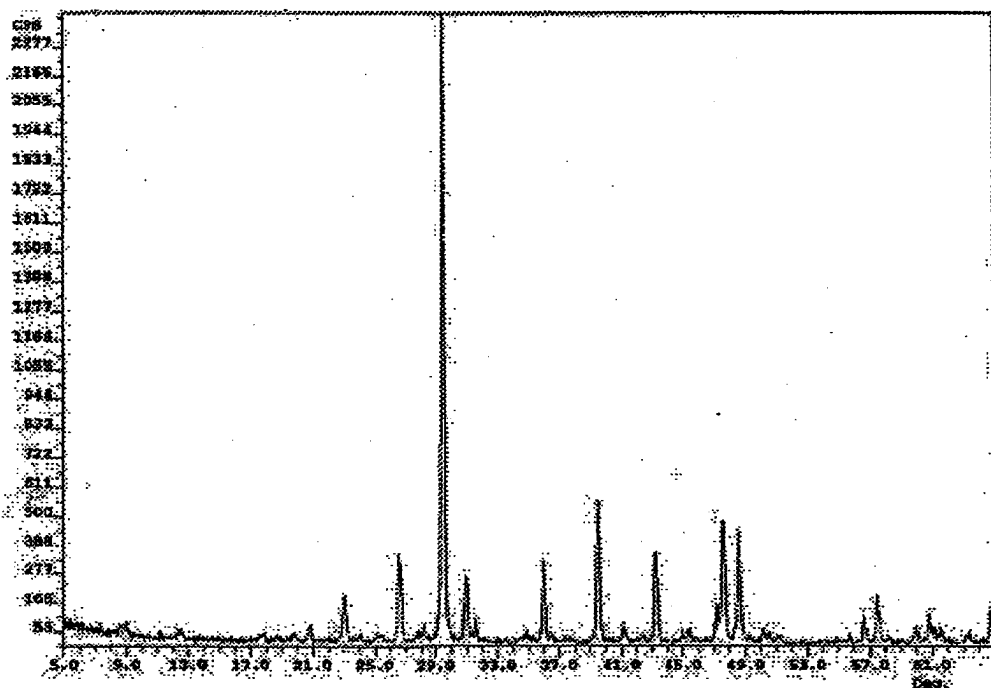


Figure 2. X-ray Diffraction Pattern of Raw Kiln Feed (5-65° 2θ, 2°/min)

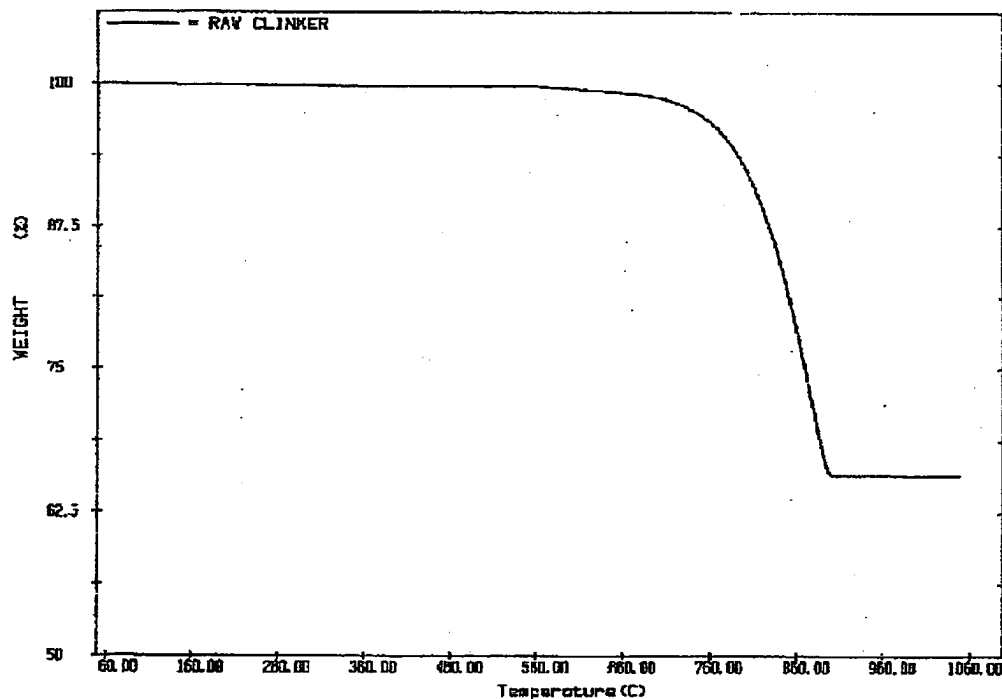


Figure 3. TGA Weight Loss Curve of Raw Kiln Feed (122-1922°F (50-1050°C), 10°C/min)

In order to study the hydraulic activity (i.e. reactivity with water) and hydration characteristics of these clinkers, isothermal calorimetry, a traditional method of studying the hydration of cement and cement-related products was used to study the rate of heat evolution of these samples. The hydration of cement produces various products one of which is calcium silicate hydrate. Calcium silicate hydrate is an amorphous material that is responsible for strength development of portland cement based products. In an isothermal calorimeter, the heat evolved during the hydration of cement is recorded with time. The resultant curve has a characteristic peak early on when water is injected into the chamber. This is due to the wetting of the various particles by the hydration medium, usually deionized water. Subsequently, when the sample undergoes a chemical reaction such as hydration, heat is either liberated (exothermic) or absorbed (endothermic). In the case of portland cement, the hydration is exothermic, and the result is shown as a reaction hump in the calorimetry curve. The area under the heat evolution curve and the timing of this reaction hump provide much information on the hydration characteristics of the sample. The suite of traces recorded for these clinkers can be used to ascertain the effectiveness of slag addition during the clinkering process.

Initially, a baseline was established using the pre-blended kiln feed. After clinkering the raw feed at various pre-selected temperatures, the product was crushed, ground, and sieved through a 325-mesh screen and x-ray diffraction patterns were collected at 2°/min 2 θ from 5° to 65°. The patterns are shown in Figures 4-7. The x-ray patterns confirm that the raw feed does not clinker well at 2012°F (1100°C) and 2192°F (1200°C). Above 2372°F (1300°C), the x-ray pattern showed successful clinkering of the raw feed into cement phases. The pattern at 2642°F (1450°C) contains peaks from calcium silicate oxide (International Committee on Diffraction Data #73-0599). The pattern from the 2372°F (1300°C) sample is essentially the same as that from the 2642°F (1450°C) sample except for the relative intensity of the peaks. As will be shown later by isothermal calorimetry, the hydration property of the 2642°F (1450°C) sample is typical of portland cement clinker. On the other hand, in addition to the calcium silicate phases, the 2012°F (1100°C) and 2192°F (1200°C) samples contained diffraction peaks from calcium oxides, the product from the release of carbon dioxide from the limestone in the raw material. The existence of calcium oxides proved that the limestone did not react completely with the other raw materials and consequently resulted in a poor cement clinker.

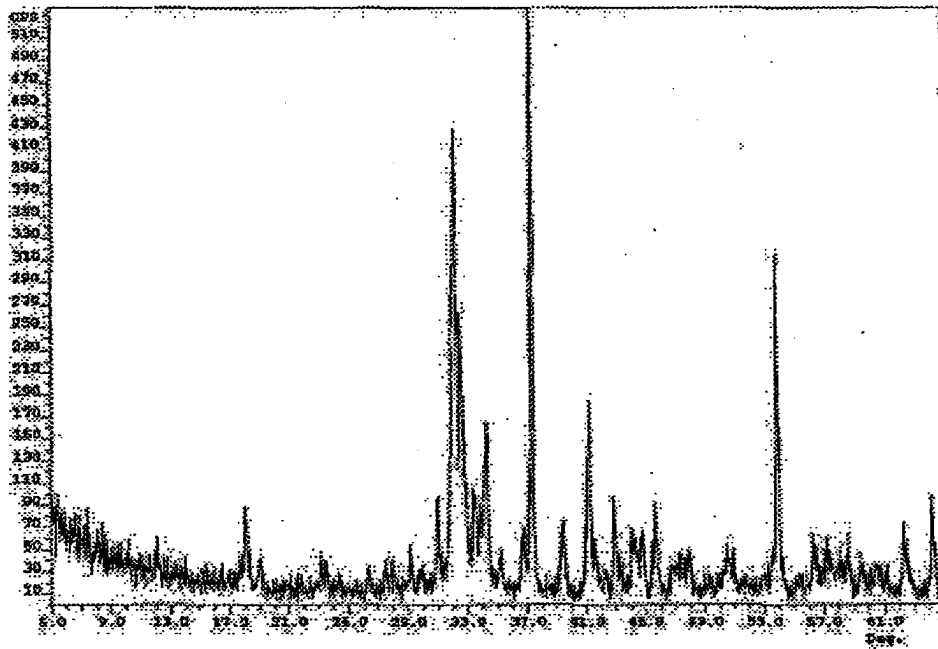


Figure 4. X-ray Diffraction Pattern of Clinker Formed at 2012°F (1100°C) (5-65° 2θ, 2°/min)

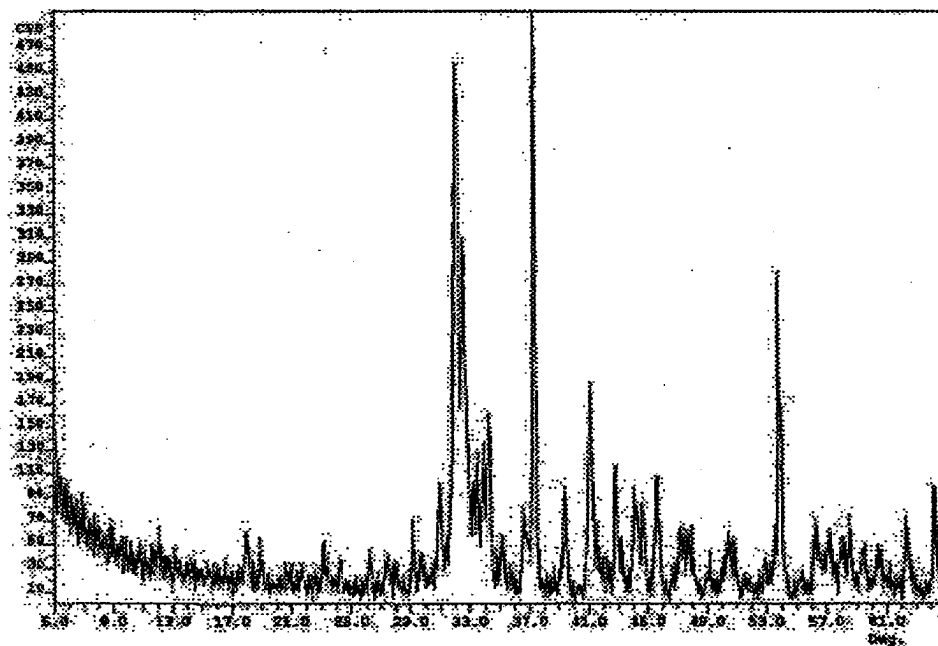


Figure 5. X-ray Diffraction Pattern of Clinker Formed at 2192°F (1200°C) (5-65° 2θ, 2°/min)

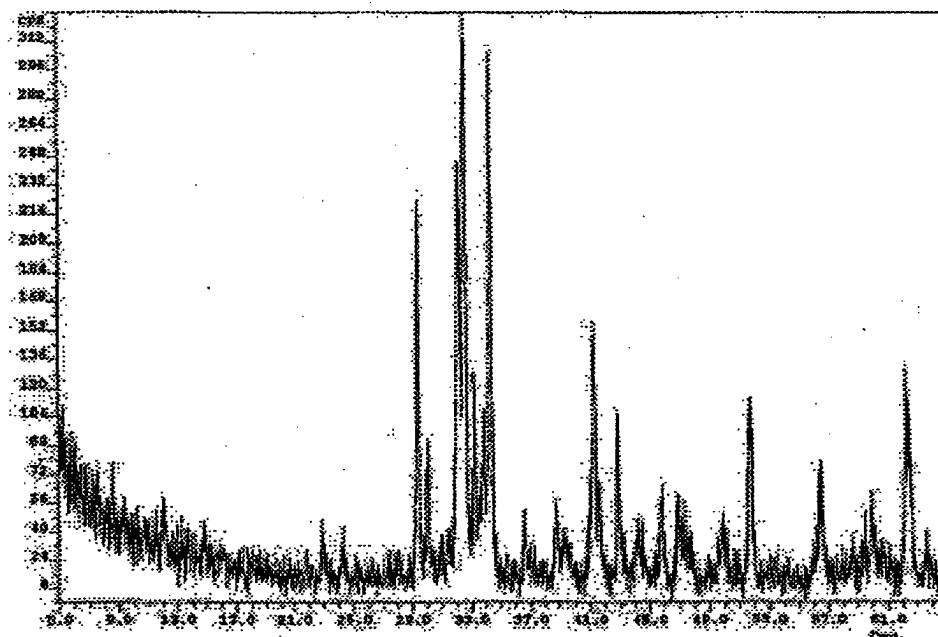


Figure 6. X-ray Diffraction Pattern of Clinker Formed at 2372°F (1300°C) (5-65° 2θ, 2°/min)

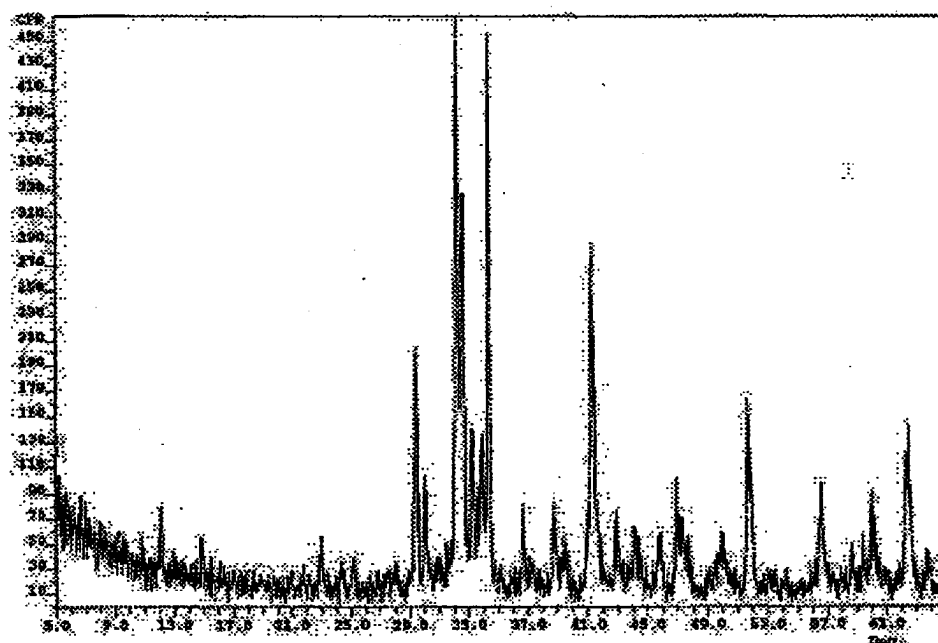


Figure 7. X-ray Diffraction Pattern of Clinker Formed at 2642°F (1450°C) (5-65° 2θ, 2°/min)

In order to study the effect of adding ground slag to the feed, prepared slag was added to the raw feed at 5% and 10% levels by weight and the resultant mixture clinkered. The addition of 5% and 10% slag to the raw feed did not alter the x-ray diffraction pattern of the material prior to the clinkering process. This was not surprising since the slag is x-ray amorphous. The x-ray pattern of the raw feed with 5% and 10% slag addition prior to clinkering are shown in Figure 8 and Figure 9. However, with the addition of the specially prepared slag to the conventional cement raw feed, the overall chemistry of the kiln feed changes. Predictions can be made using ASTM C150 based on the chemistry of the various ingredients in the kiln feed. The addition of ground slag, which is almost entirely an aluminosilicate (see chemical analysis of the slag in Sec 2.7), the expected calcium silicates in the clinker decreases dramatically. In order to compensate for the addition of the slag, limestone was added to increase the amount of expected C_3S back to about 63%. With the replacement of 10% slag for the raw feed, 30% limestone was needed to correct for the overall chemistry. This sample, consisting of 60% raw feed, 30% limestone, and 10% slag, is designated 60-30-10.

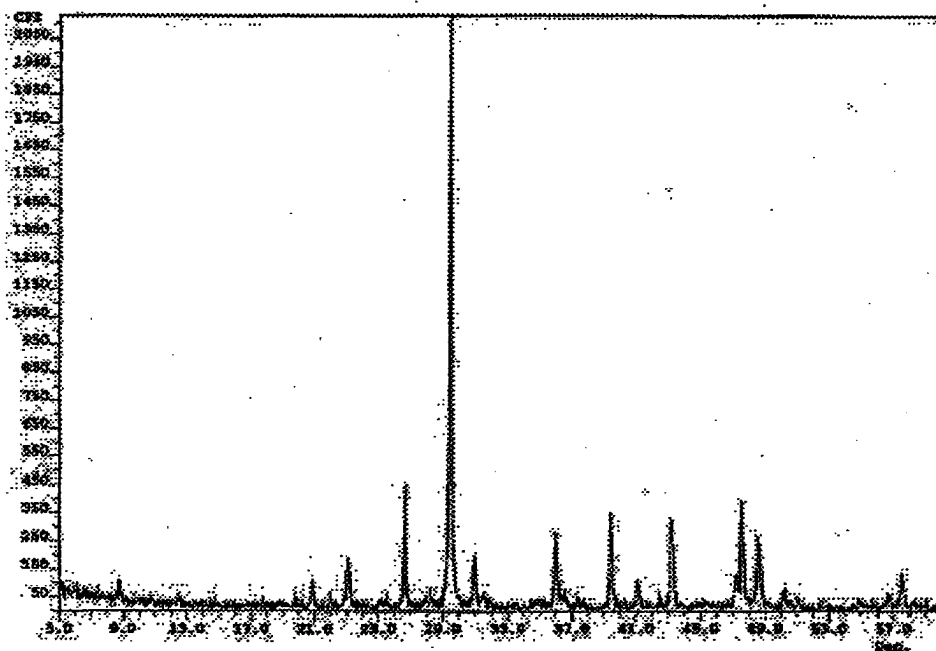


Figure 8. X-ray Diffraction Pattern of Raw Kiln Feed with 5% Ground Slag (5-65° 2 θ , 2°/min)

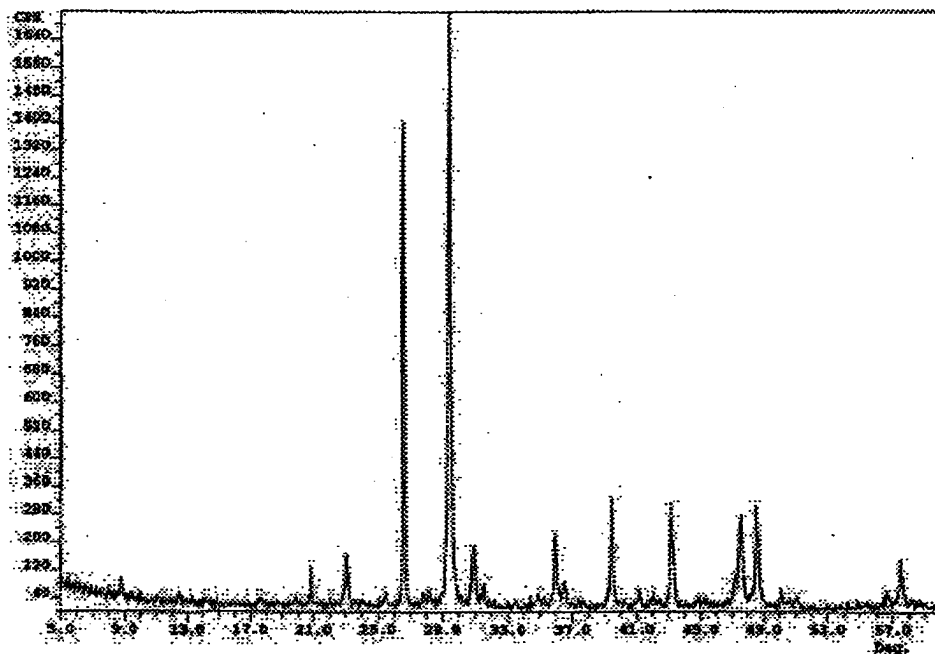


Figure 9. X-ray Diffraction Pattern of Raw Kiln Feed with 10% Ground Slag (5-65° 2 θ , 2°/min)

In order to study the hydration characteristics of the products, isothermal calorimetry of the clinker product samples was conducted at 77°F (25°C). Each sample clinker was first ground and passed through a 325 mesh sieve. Then 3 grams of material and 3 grams of deionized water (water:solids ratio of 1:1) were allowed to equilibrate inside the calorimeter separately. The sample was hydrated with the water within the calorimeter after equilibrium had been reached. Data were collected every 10 seconds up to 24 hours. Tests were conducted only on the clinkered samples and not on the raw feed since the unfired raw feed is expected to have no hydration property at all. Hydration reaction liberates heat and can be detected in very minute amount. The heat liberated (or absorbed if the reaction is endothermic) is recorded with time. The resultant heat evolution curve is indicative of the reactivity of the sample or in the case cement clinker, the relative hydraulic activity. As is typical for hydration experiments, all the heat evolution curves, shown in Figure 10, have an early initial wetting peak (in the first few minutes). At longer time, the sample that was clinkered at 2192°F (1200°C) showed no reaction peak whereas the 2642°F (1450°C) sample and the 2372°F (1300°C) (with 5% slag) showed a very pronounced reaction peak beginning at about 5 hours, lasting through almost 24 hours with the maximum at about 14 hours. Both the 2372°F (1300°C) curve and the 2642°F (1450°C) curve were very similar with the 2642°F (1450°C) curve having a slightly broader wetting curve. The 60-30-10 sample (60% raw feed, 30% limestone, and 10% ground slag) differs in that it has a much broader reaction peak centered at about 25 hours. The hydration reaction begins at about 10 hours after initial surface wetting and lasts through 40 hours. This is not unexpected given that the overall chemistry of the 60-30-10 mix results in a much higher calculated C₂S content using the Bode equation as given in ASTM C 150. Test were done at lower clinkering temperature with 10% slag but the resultant samples did not sinter properly and therefore the results not shown here. On

the basis of these calorimetry curves, it was concluded that the hydration characteristics of the sample with 5% slag clinkered at 2372°F (1300°C) are very similar to those of the sample clinkered at 2642°F (1450°C). The delayed reaction curve from the 60-30-10 sample would represent a slower reacting cement that may have special applications where a longer working time would be beneficial.

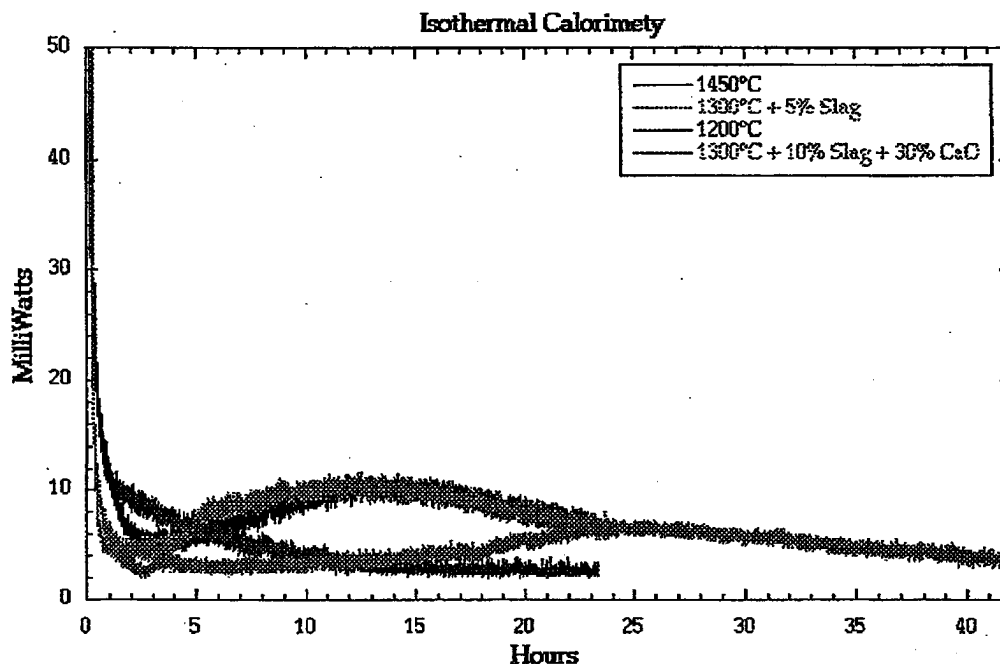


Figure 10. Isothermal Calorimetry of Clinkers Formed at Various Temperatures

X-ray diffraction analysis was used as a check of the crystalline phases present in the clinker samples; the results are shown in Figure 11. The x-ray diffraction pattern of the starting material (raw meal), and clinkers formed at 2012°F (1100°C) and 2192°F (1200°C) were included for comparison. Mineralogically, the three samples clinkered at 2642°F (1450°C), 2372°F (1300°C) using 5% slag and at 2372°F (1300°C) using 10% slag and 60% limestone are the same. This suggests that using the laboratory heating curve shown above, the same mineral phases as the raw meal can be made with slag at a lower temperature. On the other hand, the samples made at 2012°F (1100°C) and 2192°F (1200°C) clearly showed diffraction peaks from calcium oxide. This shows that the clinkering reaction was not successful at these lower temperatures.

The data from these laboratory-scale tests suggested that replacing portland cement raw meal with 5% ground slag can produce a clinker at 2372°F (1300°C) with similar hydration characteristics to a clinker produced at 2642°F (1450°C) without added slag. In addition, with the addition of limestone to correct for overall chemistry, it is possible to produce a clinker at 2372°F (1300°C) with 10% slag replacing the raw meal with the added benefit of producing a specialty slower-reacting portland cement. This suggests that a significant heat energy savings of

302°F (150°C) is possible when incorporating slag into cement kiln feed, which would translate to lower heating costs or higher kiln capacity.

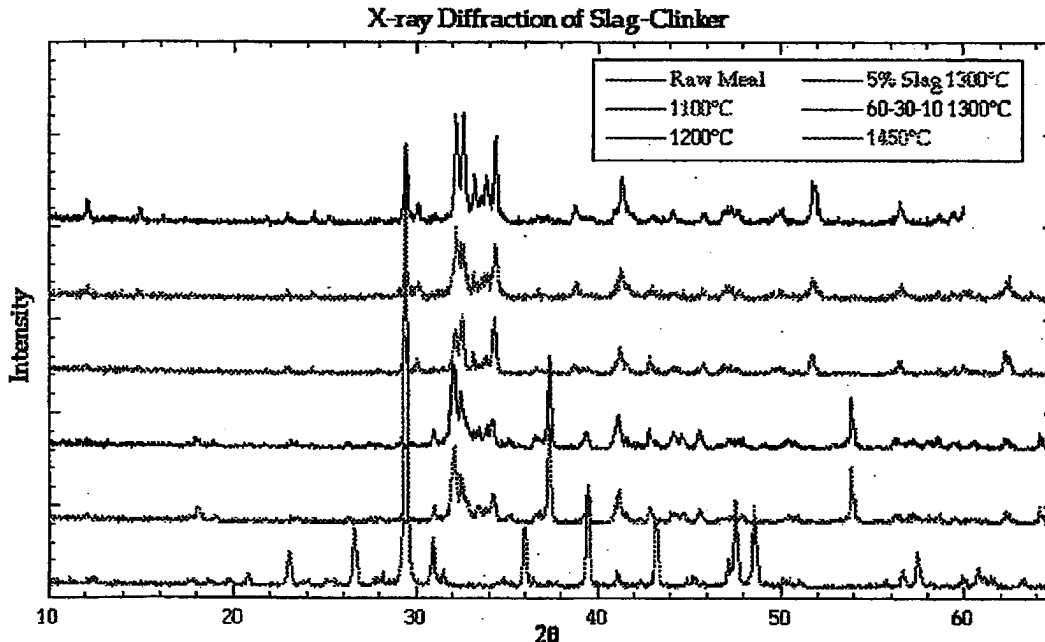


Figure 11. X-ray Diffraction Analysis of Clinkers Formed at Various Temperatures

2.6.1 Summary of Laboratory Tests

X-ray diffraction and isothermal calorimetry were used to study the characteristics of the raw cement kiln feed and clinkers made at 2012°F (1100°C), 2192°F (1200°C), 2372°F (1300°C) and 2642°F (1450°C). 5% and 10% ground slag were added to the raw feed and clinkered at 2372°F (1300°C). Limestone was added to the sample containing 10% ground slag to adjust the bulk chemistry. Data suggested that 5% and 10% addition of ground slag can produce a clinker at 2372°F (1300°C) with similar hydration characteristics to a clinker produced at 2642°F (1450°C) without added slag. However, with high dosage of ground slag, the clinker exhibited slower reactivity which may be due to a higher C_2S content. This suggests a significant heat energy saving of 302°F (150°C), which would translate to lower energy costs or higher kiln capacity. In addition to the energy savings, the slag can be used successfully as an aluminosilicate source for cement clinker.

2.7 Pilot Studies on Slag as Raw Material in Portland Cement Kiln Feed (Task 2.7)

Based on the promising results from the laboratory-scale testing at Penn State University, scale-up tests at the pilot scale was conducted at Fuller Co. to verify the lab test results using Fuller's commercial-scale equipment. A standard approach was used to evaluate the blended slag-raw meal mixes. Fuller's criteria for assessing the quality of cement clinker are based on measuring

the percent free lime in the product after clinkering samples at 2600°F (1427°C). The free lime content of a portland cement clinker is an important property. It is well known in the cement industry that excess free lime will cause long-term durability problems in portland cement-based products. In order to validate the laboratory tests done at Penn State, large batches of samples were made using the same raw meal, slag and limestone. The proportioning was based on achieving a similar chemistry to the baseline raw meal, a commercially prepared cement kiln feed. The ratio of the raw meal and limestone were adjusted in order to achieve a similar burnability index while fixing the amount of slag addition. The burnability index is a calculated value based on the overall chemistry of the mixture. This index represents the relative ability of the mixture to undergo liquid-state sintering in the cement kiln. However, since the baseline raw meal is a ready-proportioned product, it was not possible to achieve an identical overall chemistry when blending it with slag and limestone. When designing and calculating the exact mix proportion for the test burns, it was found that silica sand was needed to adjust the burnability index of the mixes. Initial tests using the pre-blended raw meal showed the addition of slag increased the percent free lime in the product clinker. Tests were conducted using 3%, 5%, and 10% slag replacement for raw meal. Appropriate quantities of limestone and silica were used such that the chemistry of the mixes matches that of a conventional Type I cement. These results are shown in Table 43 to Table 46, and summarized in Table 47.

In the case of the sample containing 3% slag and no limestone, the percent free lime at 60 minutes decreased. This is not unexpected with the addition of slag alone since it is well known that the addition of aluminosilicates decreases the free lime content of cement clinker. This may be deduced from using the Bogue equations as documented in ASTM C 150. We can treat slag as an equivalent to aluminosilicate glass as evidenced by its chemical analysis and its glass-like property. In addition, we determined that replacing the raw meal with slag without also adding limestone to the 3% mix caused the overall chemistry to change. This sample was included in order to investigate the possibility of producing a high C₂S specialty cement. However, at increased levels of slag content (5% and 10%), the free lime percentage increased very significantly. This is not desirable as the excess free lime could cause durability problems in the long run and also affects the setting behavior of the cement.

Table 43. Calculated Cement Clinker Chemistry (Pre-Blended Raw Meal, 0% Slag)

Material:	Raw Meal	Slag I	Limestone	Sand	Raw Meal	Slag I	Limestone	Sand	Pellet	Loss	Volatile	Less
	Meal	I			100.0%	0.0%	0.0%	0.0%	Feed	Free	Loss	Clinker
SiO ₂	13.64	42.48	0.70	0.00	13.64	0.00	0.00	0.00	13.64	20.70		21.24
Al ₂ O ₃ *	3.66	28.97	0.29	0.00	3.66	0.00	0.00	0.00	3.66	5.55		5.70
Fe ₂ O ₃ **	2.22	21.21	0.35	0.00	2.22	0.00	0.00	0.00	2.22	3.37		3.46
CaO	41.67	4.61	54.31	0.00	41.67	0.00	0.00	0.00	41.67	63.23		64.88
MgO	2.59	1.11	0.70	0.00	2.59	0.00	0.00	0.00	2.59	3.93		4.03
K ₂ O	0.81	1.82	0.09	0.00	0.81	0.00	0.00	0.00	0.81	1.23	1.11	0.12
Na ₂ O	0.21	0.47	0.07	0.00	0.21	0.00	0.00	0.00	0.21	0.32	0.22	0.10
SO ₃	0.84	0.62	0.08	0.00	0.84	0.00	0.00	0.00	0.84	1.27	1.21	0.06
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Loss(900°C)	34.10	-1.42	43.33	0.00	34.10	0.00	0.00	0.00	34.10	0.00		0.00
Total	99.74	99.87	99.9	0.00					99.74	99.61	2.54	99.59
Total Alkali as Na ₂ O:										1.13		0.18

Free Sulfur:	-1.3E-06	lbmol/lb feed
	-0.00011	lb/lb feed
% Sulfur Recovery:	0.00%	
K ₂ CO ₃ Required:	0	lb K ₂ CO ₃ /lb feed

Assumptions	
Volatile Losses:	
K ₂ O =	90%
Na ₂ O =	70%
SO ₃ =	95%
Cl =	100%

Calculated Cement Components			
C ₃ S =	59.42	LSF =	92.6
C ₂ S =	16.26	HM =	2.1
C ₄ A =	9.28	SR =	2.3
C ₄ AF =	10.51	AR =	1.6

Burnability Index:		3.01
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* Incl. P₂O₅ & TiO₂

** Incl. Mn₂O₃

Table 44. Calculated Cement Clinker Chemistry (Pre-Blended Raw Meal, 3% Slag)

Material:	Raw Meal	Slag I	Limestone	Sand	Raw Meal 54.0%	Slag I 5.0%	Limestone 36.5%	Sand 4.5%	0.0%	Pellet Feed	Loss Free	Volatile Loss	Volatile Less Clinker
SiO ₂	13.64	42.48	0.70	98.04	7.37	2.12	0.26	4.41	0.00	14.16	21.51		21.88
Al ₂ O ₃ *	3.66	28.97	0.29	0.06	1.98	1.45	0.11	0.00	0.00	3.53	6.37		5.46
Fe ₂ O ₃ **	2.22	21.21	0.35	0.77	1.20	1.06	0.13	0.03	0.00	2.42	3.68		3.74
CaO	41.67	4.61	54.31	0.13	22.50	0.23	19.82	0.01	0.00	42.56	64.66		65.77
MgO	2.59	1.11	0.70	0.00	1.40	0.06	0.26	0.00	0.00	1.71	2.80		2.64
K ₂ O	0.81	1.82	0.09	0.22	0.44	0.09	0.03	0.01	0.00	0.57	0.87	0.78	0.09
Na ₂ O	0.21	0.47	0.07	0.08	0.11	0.02	0.03	0.00	0.00	0.17	0.25	0.18	0.08
SO ₃	0.84	0.62	0.06	0.02	0.45	0.03	0.02	0.00	0.00	0.51	0.77	0.73	0.04
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.00	0.00	0.00	0.00
Loss(900°C)	34.10	-1.42	43.33	0.31	18.41	-0.07	15.82	0.01	0.00	34.17	0.00		0.00
Total	99.74	99.87	99.9	99.63						99.80	99.70	1.89	99.69
Total Alkali as Na ₂ O:											0.82		0.13

Free Sulfur:	-1.3E-05 lbmol/lb feed
% Sulfur Recovery:	-0.00104 lb/lb feed
K ₂ CO ₃ Required:	0 lb K ₂ CO ₃ /lb feed

Assumptions
Volatile Losses:
K ₂ O = 90%
Na ₂ O = 70%
SO ₃ = 95%
Cl = 100%

Calculated Cement Components	Type I
C ₃ S = 59.37	LSF = 91.9 (87-97)
C ₂ S = 18.11	HM = 2.1 (1.7-2.3)
C ₃ A = 8.14	SR = 2.4 (1.9-3.2)
C ₄ AF = 11.38	AR = 1.5 (1.5-2.5)

* Incl. P₂O₅ & TiO₂ ** Incl. Mn₂O₃

Table 45. Calculated Cement Clinker Chemistry (Pre-Blended Raw Meal, 5% Slag)

Material:	Raw	Slag	Limestone	Sand	Raw	Slag	Limestone	Sand		Pellet	Loss	Volatile	Volatile
	Meal	I			Meal	I							
					54.0%	5.0%	36.5%	4.5%	0.0%	Feed	Free	Loss	Clinker
SiO ₂	13.64	42.48	0.70	98.04	7.37	2.12	0.26	4.41	0.00	14.16	21.51		21.88
Al ₂ O ₃ *	3.66	28.97	0.29	0.06	1.98	1.45	0.11	0.00	0.00	3.53	5.37		5.46
Fe ₂ O ₃ **	2.22	21.21	0.35	0.77	1.20	1.06	0.13	0.03	0.00	2.42	3.68		3.74
CaO	41.67	4.61	54.31	0.13	22.50	0.23	19.82	0.01	0.00	42.56	64.66		65.77
MgO	2.59	1.11	0.70	0.00	1.40	0.06	0.26	0.00	0.00	1.71	2.60		2.64
K ₂ O	0.81	1.82	0.09	0.22	0.44	0.09	0.03	0.01	0.00	0.57	0.87	0.78	0.09
Na ₂ O	0.21	0.47	0.07	0.08	0.11	0.02	0.03	0.00	0.00	0.17	0.25	0.18	0.08
SO ₂	0.84	0.62	0.06	0.02	0.45	0.03	0.02	0.00	0.00	0.51	0.77	0.73	0.84
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Loss(900°C)	34.10	-1.42	43.33	0.31	18.41	-0.07	15.82	0.01	0.00	34.17	0.00		0.00
Total	99.74	99.87	99.9	99.63						99.80	99.70	1.89	99.69
Total Alkali as Na ₂ O:											0.82		0.13

Free Sulfur:	-1.3E-05	lbmol/lb feed
	-0.00104	lb/lb feed
% Sulfur Recovery:	0.00%	
K ₂ CO ₃ Required:	0	lb K ₂ CO ₃ /lb feed

Assumptions
Volatile Losses:
K ₂ O = 90%
Na ₂ O = 70%
SO ₃ = 95%
Cl = 100%

Calculated Cement Components	Type I
C ₃ S = 59.37	LSF = 91.9 (87-97)
C ₂ S = 18.11	HM = 2.1 (1.7-2.3)
C ₃ A = 8.14	SR = 24 (1.9-3.2)
C ₄ AF = 11.38	AR = 1.5 (1.5-2.5)

* Incl. P₂O₅ & TiO₂ ** Incl. Mn₂O₃

Table 46. Calculated Cement Clinker Chemistry (Pre-Blended Raw Meal, 10% Slag)

Material:	Raw	Slag	Limestone	Sand	Raw	Slag	Limestone	Sand		Pellet	Loss	Volatile	Volatile	
	Meal	I			Meal	I								Less
SiO ₂	13.64	42.48	0.70	98.04	1.43	4.25	0.50	8.33	0.00	14.51	22.06		22.26	
Al ₂ O ₃ *	3.66	28.97	0.29	0.06	0.38	2.90	0.21	0.01	0.00	3.49	5.31		5.36	
Fe ₂ O ₃ **	2.22	21.21	0.35	0.77	0.23	2.12	0.25	0.07	0.00	2.67	4.06		4.09	
CaO	41.67	4.61	54.31	0.13	4.38	0.46	38.56	0.01	0.00	43.41	66.00		66.59	
MgO	2.59	1.11	0.70	0.00	0.27	0.11	0.50	0.00	0.00	0.88	1.34		1.35	
K ₂ O	0.81	1.82	0.09	0.22	0.09	0.18	0.06	0.02	0.00	0.35	0.53	0.48	0.05	
Na ₂ O	0.21	0.47	0.07	0.08	0.02	0.05	0.05	0.01	0.00	0.13	0.19	0.13	0.06	
SO ₃	0.84	0.62	0.06	0.02	0.09	0.06	0.04	0.00	0.00	0.19	0.30	0.28	0.01	
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Loss(900°C)	34.10	-1.42	43.33	0.31	3.58	-0.14	30.76	0.03	0.00	34.23	0.00		0.00	
Total	99.74	99.87	99.9	99.63						99.86	99.78	0.89	99.78	
Total Alkali as Na ₂ O:											0.54		0.09	

Free Sulfur:	-2E-05	lbmol/lb feed
	-0.002	lb/lb feed
% Sulfur Recovery:	0.00%	
K ₂ CO ₃ Required:	0	lb K ₂ CO ₃ /lb feed

Assumptions		
Volatile Losses:		
K ₂ O =	90%	
Na ₂ O =	70%	
SO ₃ =	95%	
Cl =	100%	

Calculated Cement Components			Type I
C ₃ S =	59.99	LSF =	91.7 (87-97)
C ₂ S =	18.75	HM =	2.1 (1.7-2.3)
C ₃ A =	7.28	SR =	2.4 (1.9-3.2)
C ₄ AF =	12.44	AR =	1.3 (1.5-2.5)
Burnability Index:		3.04	

* Incl. P₂O₅ & TiO₂ ** Incl. Mn₂O₃

* Incl. P₂O₅ & TiO₂ ** Incl. Mn₂O₃

Table 47. Summary of Free Lime Tests Using Pre-Blended Cement Kiln Raw Meal

Temp = 2600°F (1427°C)	Raw Meal	3% Slag	5% Slag + Limestone	10% Slag + Limestone
% Free Lime at 60 minutes	0.35	0.15	0.54	0.85
Burnability Index	3.01	1.37	3.04	3.04

In order to further quantify the effects of using slag as a partial replacement for raw meal in making portland cement clinker, Fuller Co. acquired a very hard-burning raw meal, consisting of limestone, sandstone, shale, and iron, this time in component form instead of as a pre-blended raw meal. A hard-burning mix is a cement mix for which it is very difficult to produce the liquid phase in the kiln. Hard-burning mixes usually require both higher temperatures and longer residence times during the clinkering process.

We hypothesized that using a hard-burning mix would allow us to more easily detect whether the slag would perform as a fluxing agent, increasing the liquid phase in the kiln and therefore making the mixture easier to burn. Combining the various components in the appropriate ratios also made it much easier to adjust the bulk chemistry of the raw material when slag was used. Free lime tests were conducted at 0%, 3%, 5% and 8.5% levels of slag replacement (see Tables 49-52). The baseline mix (with no slag) was proportioned according to the manufacturer's specifications conforming to specifications of a Type I portland cement. Using these raw materials, we determined that the maximum amount of slag that can be added while retaining the same baseline initial chemistry was 8.5%.

Table 48. Calculated Cement Clinker Chemistry (Component Raw Ingredients, 0% Slag)

Material:	Lime-stone	Sand-stone	Shale	Iron	Slag I	Lime-stone 82.7%	Sand-stone 6.3%	Shale 10.0%	Iron 1.0%	Slag I 0.0%	Pellet Feed	Loss Free	Volatiles Loss	Volatiles Less Clinker
SiO ₂	3.49	91.57	56.18	2.31	42.48	2.89	5.77	5.62	0.02	0.00	14.30	22.03		22.26
Al ₂ O ₃ *	1.25	3.15	24.12	0.56	28.97	1.03	0.20	2.41	0.01	0.00	3.65	5.63		5.68
Fe ₂ O ₃ **	0.53	0.84	7.34	100.29	21.21	0.44	0.05	0.73	1.00	0.00	2.23	3.43		3.47
CaO	51.54	1.48	1.63	0.63	4.61	42.62	0.09	0.16	0.01	0.00	42.89	66.10		66.77
MgO	0.93	0.02	0.71	0.00	1.11	0.77	0.00	0.07	0.00	0.00	0.84	1.30		1.31
K ₂ O	0.41	0.42	0.98	0.03	1.82	0.34	0.03	0.10	0.00	0.00	0.46	0.71	0.64	0.07
Na ₂ O	0.09	0.09	0.74	0.18	0.47	0.07	0.01	0.07	0.00	0.00	0.16	0.24	0.17	0.07
SO ₃	0.04	0.05	0.08	0.07	0.62	0.03	0.00	0.01	0.00	0.00	0.04	0.07	0.07	0.00
Cl	0.01	0.10	0.62	0.62	0.00	0.01	0.01	0.06	0.01	0.00	0.08	0.13	0.13	0.00
Loss(900°C)	41.42	2.23	7.80	-5.50	-1.42	34.25	0.14	0.78	-0.06	0.00	35.12	0.00		0.08
Total	99.71	99.95	100.2	99.19	99.87						99.77	99.64	1.00	99.64
Total Alkali as Na₂O:												0.71		0.12

Free Sulfur:	-4.5E-05 lbmol/lb feed
	-0.0036 lb/lb feed
% Sulfur Recovery:	0.00%
K ₂ CO ₃ Required:	0 lb K ₂ CO ₃ /lb feed

Assumptions
Volatiles Losses:
K ₂ O = 90%
Na ₂ O = 70%
SO ₃ = 95%
Cl = 100%

Calculated Cement Components	Type I
C ₃ S = 59.45	LSF = 91.58 (87-97)
C ₂ S = 19.16	HM = 2.13 (1.7-2.3)
C ₃ A = 9.20	SR = 2.43 (1.9-3.2)
C ₄ AF = 10.55	AR = 1.64 (1.5-2.5)
Burnability Index: 3.01	

* Incl. P₂O₅ & TiO₂ ** Incl. Mn₂O₃

Table 49. Calculated Cement Clinker Chemistry (Component Raw Ingredients, 3% Slag)

Material	Lime- stone	Sand- stone	Shale	Iron	Slag I	Lime- stone 80.2%	Sand- stone 6.1%	Shale 9.7%	Iron 1.0%	Slag I 3.0%	Pellet Feed	Loss Free	Volatile Loss	Volatile Less Clinker
SiO ₂	3.49	91.57	56.18	2.31	42.48	2.80	5.60	5.45	0.02	1.27	15.14	22.95		23.20
Al ₂ O ₃ *	1.25	3.15	24.12	0.56	28.97	1.00	0.19	2.34	0.01	0.87	4.41	6.68		6.76
Fe ₂ O ₃ **	0.53	0.84	7.34	100.29	21.21	0.43	0.05	0.71	0.97	0.64	2.80	4.24		4.29
CaO	51.54	1.48	1.63	0.63	4.61	41.34	0.09	0.16	0.01	0.14	41.74	63.26		63.95
MgO	0.93	0.02	0.71	0.00	1.11	0.75	0.00	0.07	0.00	0.03	0.85	1.29		1.30
K ₂ O	0.41	0.42	0.98	0.03	1.82	0.33	0.03	0.10	0.00	0.05	0.50	0.76	0.69	0.08
Na ₂ O	0.09	0.09	0.74	0.18	0.47	0.07	0.01	0.07	0.00	0.01	0.17	0.25	0.18	0.08
SO ₃	0.04	0.05	0.08	0.07	0.62	0.03	0.00	0.01	0.00	0.02	0.06	0.09	0.09	0.00
Cl	0.01	0.10	0.62	0.62	0.00	0.01	0.01	0.06	0.01	0.00	0.08	0.12	0.12	0.00
Loss(900°C)	41.42	2.23	7.80	-5.50	-1.42	33.23	0.14	0.76	-0.05	-0.04	34.02	0.00		0.00
Total	99.71	99.95	100.2	99.19	99.87						99.77	99.65	1.07	99.65
												Total Alkali as NaO:	0.75	0.13

Free Sulfur:	-4.8E-05 lbmol/lb feed
% Sulfur Recovery:	-0.00386 lb/lb feed
K ₂ CO ₃ Required:	0 lb K ₂ CO ₃ /lb feed

Assumptions
Volatile Losses:
K ₂ O = 90%
Na ₂ O = 70%
SO ₃ = 95%
Cl = 100%

Calculated Cement Components	Type I
C ₃ S = 32.43	LSF = 82.40 (87-97)
C ₂ S = 42.28	HM = 1.87 (1.7-2.3)
C ₄ A = 10.66	SR = 2.10 (1.9-3.2)
C ₄ AF = 13.03	AR = 1.58 (1.5-2.5)
Burnability Index: 1.37	

* Incl. P₂O₅ & TiO₂ - ** Incl. Mn₂O₃

Table 50. Calculated Cement Clinker Chemistry (Component Raw Ingredients, 5% Slag)

Material:	Lime- stone	Sand- stone	Shale	Iron	Slag I	Lime- stone	Sand- stone	Shale	Iron	Slag I	Pellet Feed	Loss Free	Volatile Loss*	Volatile Less Clinker
	82.9%	7.7%				4.0%	0.4%							5.0%
SiO ₂	3.49	91.57	56.18	2.31	42.48	2.89	7.05	2.25	0.01	2.12	14.32	21.95		22.17
Al ₂ O ₃ *	1.25	3.15	24.12	0.56	28.97	1.04	0.24	0.96	0.00	1.45	3.69	5.66		5.72
Fe ₂ O ₃ **	0.53	0.84	7.34	100.29	21.21	0.44	0.06	0.29	0.40	1.06	2.26	3.46		3.50
CaO	51.54	1.48	1.63	0.63	4.61	42.73	0.11	0.07	0.00	0.23	43.14	66.09		66.76
MgO	0.93	0.02	0.71	0.00	1.11	0.77	0.00	0.03	0.00	0.06	0.86	1.31		1.33
K ₂ O	0.41	0.42	0.98	0.03	1.82	0.34	0.03	0.04	0.00	0.09	0.50	0.77	0.69	0.08
Na ₂ O	0.09	0.09	0.74	0.18	0.47	0.07	0.01	0.03	0.00	0.02	0.14	0.21	0.15	0.06
SO ₃	0.04	0.05	0.08	0.07	0.62	0.03	0.00	0.00	0.00	0.03	0.07	0.11	0.10	0.01
Cl	0.01	0.10	0.62	0.62	0.00	0.01	0.01	0.02	0.00	0.00	0.04	0.07	0.07	0.00
Loss(900°C)	41.42	2.23	7.80	-5.50	-1.42	34.34	0.17	0.31	-0.02	-0.07	34.73	0.00		0.00
Total	99.71	99.95	100.2	99.19	99.87						99.75	99.62	1.01	99.62
Total Alkali as Na ₂ O:												0.71		0.11

Free Sulfur:	-4.871E-05	lbmol/lb feed
	-0.003897	lb/lb feed
% Sulfur Recovery:	0.00%	
K ₂ CO ₃ Required:	-0	lb K ₂ CO ₃ /lb feed

Assumptions
Volatile Losses:
K ₂ O = 90%
Na ₂ O = 70%
SO ₃ = 95%
Cl = 100%

Calculated Cement Components				Type I
C ₃ S = 59.82	LSF = 91.8	91.8	(87-97)	
C ₂ S = 18.63	HM = 2.1	2.1	(1.7-2.3)	
C ₃ A = 9.24	SR = 2.4	2.4	(1.9-3.2)	
C ₄ AF = 10.63	AR = 1.6	1.6	(1.5-2.5)	

* Incl. P₂O₅ & TiO₂ ** Incl. Mn₂O₃

* Incl. P₂O₅ & TiO₂ ** Incl. Mn₂O₃

Table 51. Calculated Cement Clinker Chemistry (Component Raw Ingredients, 8.5% Slag)

Material:	Lime-stone	Sand-stone	Shale	Iron	Slag	Lime-stone	Sand-stone	Shale	Iron	Slag	Pellet	Loss	Volatiles	Less
						83.0%	8.5%	0.0%	0.0%	8.5%	Feed	Free	Loss	Clinker
SiO ₂	3.49	91.57	56.18	2.31	42.48	2.90	7.78	0.00	0.00	3.61	14.29	21.80		22.02
Al ₂ O ₃ *	1.25	3.15	24.12	0.56	28.97	1.04	0.27	0.00	0.00	2.46	3.77	5.75		5.81
Fe ₂ O ₃ **	0.53	0.84	7.34	100.29	21.21	0.44	0.07	0.00	0.00	1.80	2.31	3.53		3.57
CaO	51.54	1.48	1.63	0.63	4.61	42.78	0.13	0.00	0.00	0.39	43.30	66.05		66.73
MgO	0.93	0.02	0.71	0.00	1.11	0.77	0.00	0.00	0.00	0.09	0.87	1.32		1.34
K ₂ O	0.41	0.42	0.98	0.03	1.82	0.34	0.04	0.00	0.00	0.15	0.53	0.81	0.73	0.08
Na ₂ O	0.09	0.09	0.74	0.18	0.47	0.07	0.01	0.00	0.00	0.04	0.12	0.19	0.13	0.06
SO ₂	0.04	0.05	0.08	0.07	0.62	0.03	0.00	0.00	0.00	0.05	0.09	0.14	0.13	0.01
Cl	0.01	0.10	0.62	0.62	0.00	0.01	0.01	0.00	0.00	0.00	0.02	0.03	0.03	0.00
Loss(900°C)	41.42	2.23	7.80	-5.50	-1.42	34.38	0.19	0.00	0.00	-0.12	34.45	0.00		0.00
Total	99.71	99.95	100.2	99.19	99.87						99.74	99.61	1.02	99.60
Total Alkali as Na ₂ O:												0.72		0.11

Free Sulfur:	-5.14E-05 lbmol/lb feed
	-0.004115 lb/lb feed
% Sulfur Recovery:	0.00%
K ₂ CO ₃ Required:	-0 lb K ₂ CO ₃ /lb feed

Assumptions
Volatiles Losses:
K ₂ O = 90%
Na ₂ O = 70%
SO ₂ = 95%
Cl = 100%

Calculated Cement Components	Type I
C ₂ S = 60.07	LSF = 92.0 (87-97)
C ₃ S = 18.03	HM = 2.1 (1.7-2.3)
C ₄ A = 9.36	SR = 2.3 (1.9-3.2)
C ₂ AF = 10.84	AR = 1.6 (1.5-2.5)

* Incl. P₂O₅ & TiO₂ ** Incl. Mn₂O₃

The free lime test results are summarized in Table 52. The hard-burning mix we used initially had a free lime content of 2.86% in 60 minutes of burn time at 2600°F (1427°C.) With the addition of 5% slag, the free lime content increased to 4.92%. This level, which was significantly higher than that of the initial baseline mix, was deemed unsatisfactory and further tests were abandoned.

Table 52. Summary of Free Lime Test Using Raw Ingredients

Temp = 2600°F (1427°C)	Initial Hard Burn Mix	3% Slag	5% Slag	8.5% Slag
Burnability Index	3.01	1.37	3.01	2.97
% Free Lime at 60 minutes	2.86	Being analyzed	4.92	Being analyzed

We then contacted a number of cement manufacturers and they all said that they would never use such a hard-burning mix since the silica modulus is too high. As an added test, the silica modulus was therefore adjusted to a more common value once again using raw ingredients. The resultant percent free lime from tests burns are shown in Table 53.

Table 53. Summary of Free Lime Test Using Raw Ingredients with Lower Silica Modulus

Temp = 2600°F (1427°C)	Initial Hard Burn Mix with lower silica modulus	3% Slag	5% Slag	8.5% Slag
% Free Lime at 60 minutes	0.19	0.17	0.18	0.60

Using a blend with a more conventional silica modulus, the initial baseline test resulted in a free lime of 0.19% after 1 hour. With 3% or 5% slag replacement, although there was a very slight decrease of free lime to 0.17% and 0.18% respectively, the advantage is minimal. Finally, the mixture containing 8.5% slag had a free lime content of 0.60% after 1 hour, which is an unacceptably high value. We therefore concluded that, contrary to the initial laboratory-scale tests, slag did not perform well as a fluxing agent and consequently did not appreciably decrease the percent free lime of the cement clinker. Although using a small quantity of slag as a feed material is beneficial from the viewpoint of waste utilization, it neither proved to assist in producing a better quality cement clinker nor significantly reduced costs.

2.8 Pozzolonic Activity of Prepared Gasifier Slag

The test work under this subtask focused on utilizing the property of gasification slag that is similar to that of an aluminosilicate glass. It is well known that certain types of fly ash can be used as a pozzolan in cement systems. Pozzolans have the unique property that, when combined with lime in a relatively high pH environment, they tend to form calcium silicate hydrate at a later time. As noted before, calcium silicate hydrate is the major binding phase of portland cement-based systems and is responsible for the strength development of these systems. With the addition of pozzolans, the resultant blended cement will usually have better mechanical properties over the long term and also, more importantly, better durability. The increase in durability is the result of the ability of pozzolans to tie up free lime and other undesirables such as alkalis that would otherwise cause durability problems with the cement. In terms of overall chemistry, slag is similar to Class F coal fly ash, which is well known to be a good pozzolan. Although mineralogically slag is completely different from Class F fly ash, their similarity in overall chemistry makes slag a viable candidate as a pozzolan. Therefore, tests were conducted to evaluate the pozzolonic activity of gasifier slag with the intention of using it as a blended material in cement. Two ASTM tests were used to examine the suitability of slag as a pozzolan. The tests are:

- ASTM C 311: Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland Cement Concrete
- ASTM C 593: Fly Ash and Other Pozzolans for Use with Lime.

As indicated by the ASTM tests, these are two different applications. Fine ground slag was prepared and tested according to the ASTM standards. The results for each test are shown in Table 54 and Table 55 respectively.

Table 54. ASTM C 311 Results Using Specially Prepared Slag

	OPC	35% Slag Replacement
28-day compressive strength (psi)	3,948	5,489
Pozzolonic activity	100%	139%

As shown in Table 54, finely ground slag was indeed a very good pozzolan with a pozzolonic index of 139%. The compressive strength of the baseline sample using ordinary portland cement

(OPC) was slightly less than 4,000 psi after 28 days of curing. With 35% replacement of OPC by slag, the compressive strength increased dramatically to just under 5,500 psi after 28 days of curing.

Slag was also tested according to ASTM C 593 and the results are shown in Table 55.

Table 55. ASTM C 593 Results Using Specially Prepared Slag

	Minimum Requirement	Test Sample
7-day compressive strength, psi	600	1,104
28-day compressive strength, psi	600	1,326

The compressive strength of the slag samples as tested according to ASTM C 593 was excellent and far exceeded the ASTM requirement.

It is evident from these tests that finely ground gasifier slag is indeed a good pozzolan and may be used beneficially in portland cement blends.

In order to further quantify the pozzolanic effect of ground slag and its relations to particle size, additional tests were conducted both at Fuller Co. and Penn State University. A quantity of slag in storage at Fuller Co. was ground to -200 mesh and -325 mesh nominal, respectively, and the Bond Ball Mill Grindability Test was performed on these two samples. This is a standard ball mill test used to determine the relative power requirements for grinding various materials. Prior to testing, the slag was ground to -6 mesh. The initial particle size distribution is shown in Table 56.

Table 56. Initial Particle Size Distribution of Slag Prior to Bond Ball Mill Grindability Test

Size	Passing
6 M	100%
8 M	64.5%
12 M	21.9%
16 M	9.7%
20 M	6.1%
30 M	4.2%
40 M	3.0%
50 M	2.1%
70 M	1.4%
100 M	0.9%
140 M	0.6%
170 M	0.5%
200 M	0.4%
325 M	0.2%

The results of the grinding test are shown in Table 57.

Table 57. Slag Bond Ball Mill Grindability Test Results

	Blaine Surface Area	BWI*
-200 M Grind	1592 m ² /g	22.8 kw/mt
-325 M Grind	2558 m ² /g	27.9 kw/mt
** Typical cement clinker	~3800 m ² /g	13-15 kw/mt

*BWI: Bond Work Index, which represents the energy required for grinding.

** Typical cement clinker shown here for comparison.

The BWI of the ground slag was higher than that of a typical cement clinker. The higher BWI characteristic of gasifier slag may be attributed to its crystal size. If the crystal size of the gasifier slag is larger than that of cement clinker despite other physical properties being similar, it will take considerably more power to grind the slag to a similar Blaine. Grinding aides were not used when determining the BWI. If the higher BWI of the slag is attributed to its crystal size, grinding aides may not provide much of a benefit. On the other hand, since the slag is slightly magnetic, if the magnetic properties of the material affect flow in the mill and reduce the grinding effectiveness of the mill charge, the addition of a grinding aide may help. Slags are generally harder to grind. A large percentage of cement producers use steel slag in their raw materials, and steel slag often has a BWI of >20.

The Sedigraph Particle Size Distribution of the ground slags is shown in Table 58.

Table 58. Sedigraph Particle Size Distribution of Ground Slag

Cumulative % Passing		
	200 mesh	325 mesh
Microns	Grind	Grind
75	100	100
53	77.8	100
45	66.3	100
32	47.1	82.5
25	36.1	66
20	27.9	52.6
15	20.5	39.2
10	13	25.7
6	6.4	14.2
5	5.1	11.5
4	3.6	9.2
3	2.3	6.6
2	1	4.6
1	0	2.5

The -200 mesh material was subjected to ASTM C 311 and C 593 tests and the results are shown in Table 59 and Table 60.

Table 59. ASTM C 311 Results Using -200 Mesh Ball Milled Slag

	OPC	35% Slag Replacement
28-day compressive strength, psi	3,948	3084
Pozzolanic activity	100%	-8.64%

Table 60. ASTM C 593 Results Using -200 Mesh Ball Milled Slag

	Minimum Requirement	Test Sample
7-day compressive strength, psi	600	987.5
28-day compressive strength, psi	600	813.3

As shown in Tables 54 and 55, gasifier slag can indeed be a very good pozzolan and deserves more in-depth studies. However, conventional ball milling may not be the best method for grinding this material. ASTM C 311 test results showed that -200 mesh ball-milled slag was not a very effective pozzolan with a pozzolanic activity of -8.64%. However, the -200 mesh ball-milled slag did pass the ASTM C 593 test, albeit not spectacularly. The processing (grinding) of gasifier slag into an effective pozzolan in a low-cost manner is not trivial and requires further experimentation and testing.

3.0 FINAL AND OTHER REPORTS

All project reports, including quarterly technical and financial status reports, were submitted in a timely fashion. Topical Report No. 1, which constituted a summary of the Phase I work, was submitted in May 1996. The subject report is Topical Report No. 2 and represents the Final Technical Report for the project.

4.0 CONCLUSIONS AND RECOMMENDATIONS

4.1 General Conclusions

Separation and recovery of char from slag using the process developed by Praxis Engineers, Inc. was demonstrated successfully under this program. Since the char (unconverted carbon) present in gasification slag constitutes a hindrance to its utilization, its removal is a critical step in the development of utilization applications for slag. The results show that the Praxis process is effective in separating the char from the slag to yield a char-free slag product. The char-free slag can be sold as a substitute for several conventional aggregates used in high-volume applications.

Demonstration of the char separation process was followed by successful demonstration of the production of lightweight aggregates (LWA) and ultra-lightweight aggregates (ULWA) from slag at the pilot scale, using technology developed by Praxis. It was demonstrated that slag can also be blended with conventional expansive shale and clays to produce LWAs.

The slag samples used in the program were generated from two different gasification processes namely, those used by Destec and Texaco, each of which uses different bituminous coals. Thus the char separation and expanded slag production processes demonstrated during the project can be generalized to apply to most of the coals or gasification processes in current application in the United States. This includes the Tampa Electric and Wabash River Repowering IGCC projects co-funded by DOE.

All of the project slag samples tested expanded at temperatures ~400°F lower than those required for pyroprocessing of expansive shales and clays. This represents significant savings in pyroprocessing fuel energy requirements. In all of the types of expansion processes that were demonstrated, sufficient control of the product unit weight as a function of temperature was possible to produce LWAs and ULWAs. However, ULWAs produced using slag had unit weights of about 18 lb/ft³, which is considerably higher than those made from perlite which are typically in the 4-12 lb/ft³ range. Nevertheless, it is important to note that the compressive strength of the slag-based ULWAs was also correspondingly higher. High strength, even though accompanied by high unit weight, was identified as a very useful property in several applications.

Extensive testing was performed to establish the potential for utilization of expanded slag aggregates in the 18-60 lb/ft³ unit weight range in two distinct types of target applications:

1. **Conventional LWA Applications:** Expanded slags were successfully tested as total and partial substitutes for several conventional LWA applications, namely structural lightweight concrete, masonry blocks (CMUs), lightweight roof tiles and concrete panels (Wonderboard). It was concluded that expanded slag products meet the requirements for these lightweight aggregate applications. These applications use conventional LWAs in the 50-55 lb/ft³ unit weight range which sell for ~\$50/ton. Since some of these applications could benefit from using aggregates with even lower unit weights, we used expanded slag in the 40-55 lb/ft³ range to test these applications.

2. **Conventional ULWA Applications:** Expanded slags were successfully tested as total and partial substitutes for several conventional ULWA applications, namely insulating concrete, loose fill insulation, and nursery/horticultural applications. Perlite-based ULWAs in the $<4\text{--}12\text{ lb/ft}^3$ unit weight range sell for $\sim\$200/\text{ton}$. Since the slag could only achieve a unit weight of 18 lb/ft^3 at the pilot scale, tests were conducted using this material to evaluate its comparative performance in these applications. It was concluded that this SLA meets some of the requirements for expanded perlite. However, optimal results were obtained when expanded slag was used as a partial substitute for perlite products.

4.2 Specific Conclusions from Applications Testing

Expanded slags were successfully tested as total and partial substitutes for several LWA and ULWA applications. The findings are summarized below.

4.2.1 Lightweight Aggregate Applications

LWA applications tested included lightweight roof tiles, lightweight blocks, structural concrete, and concrete panels. The findings for these applications are discussed below.

1. **Lightweight Roof Tiles.** Lightweight concrete roof tiles are being increasingly used on the West Coast and Florida because of their high fire rating, durability, and aesthetic appeal. The ASTM requirement for lightweight concrete is a compressive strength of 5,000 psi with a unit weight of $<108\text{ lb/ft}^3$ using a typical cement-to-aggregate ratio of 1:2.5. Two additives (a superplasticizer and an accelerator) are commonly used. Using an identical mix, the test results confirmed that ASTM and industry requirements were met for this application. In fact, a lower-unit-weight slag ($<55\text{ lb/ft}^3$) may be used to produce slightly lighter tiles. Large-scale production and testing of SLA-based roof tiles could not be accomplished due to plant unavailability.
2. **Lightweight Blocks (CMUs).** Expanded slag aggregates were successfully tested for production of lightweight blocks. The target lightweight block product (8" CMU) weighs $<27\text{ lb}$ on a dry basis. The ASTM and industry requirements for concrete used for this application include a compressive strength of 2,000 psi at a unit weight of $<115\text{ lb/ft}^3$, using a typical cement-to-aggregate ratio of $<1:5$. Commercial production of the lightweight blocks was accomplished successfully at a commercial manufacturing plant. We produced 250 blocks using the conventional block mix and the same materials (sand, cement, and fillers) currently used by the plant. SLA was used to replace the conventional LWA, and constituted 44% of the total aggregates by volume in the mix. In the production of slag LWA blocks, the entire automated production and post-production manufacturing process line was used without modification. The green CMUs were handled through the processing steps without any problems, and no special curing or handling requirements were needed. The product met both industry and ASTM requirements. SLA has an excellent potential to replace or complement the existing LWA for this application. The plant would use the SLA if its delivered price were lower than the price paid for LWA.

3. **Structural Concrete.** Structural concrete is used in the construction of high-rise buildings and bridges. Expanded slag was successfully used to make structural concrete that met ASTM and industry requirements of compressive strengths of 2,500-4,000 psi for sand LWA concrete with unit weights in the 105-115 lb/ft³ range, using a typical industry cement-to-aggregate ratio of 1:4. SLA used as a partial replacement for clay-based aggregates produced concrete with an even higher strength of 5500 psi.
4. **Concrete Panels.** Concrete panels (Wonderboard) are used for structural reinforcement and as water-resistant backing for ceramic tile installations. The target specification for concrete for this application was the industry requirement of a compressive strength of 2,500 psi with a panel weight of 3.2-3.6 lb/ft² using a cement-to-aggregate ratio of 1:2.5. Tests conducted at the facility of a panel manufacturer demonstrated that expanded slag in the 35-40 lb/ft³ unit weight range met their requirements and may even perform better than the conventional materials due to its lower unit weight. The panel manufacturer requested a quotation for supplying the expanded slag material with the intention of procuring a minimum of 20,000 tons/day of SLA products for one plant. They were also interested in participating in a joint venture to set up an SLA production facility to meet their increasing demand.

4.2.2 Ultra-lightweight Aggregate Applications

ULWA applications tested included insulating concrete, loose fill insulation, and nursery/horticultural applications. The findings for these applications are discussed below.

1. **Insulating Concrete.** Insulating concrete is used as an insulating top layer in built-up roofs and is typically manufactured using expanded perlite or shale. The application requires a 200-psi concrete. ASTM insulation requirement (thermal conductivity) for shale-based products with unit weights in the 50-90 lb/ft³ range is 1.5-3.0 Btu-in/h-ft²-°F. For a perlite-based product (15-50 lb/ft³ unit weight) the thermal conductivity required is 0.45-1.5 Btu-in/h-ft²-°F. In comparison, SLA concrete at a unit weight of 45.1 lb/ft³ had a thermal conductivity of 0.98 Btu-in/h-ft²-°F. The thermal conductivity of SLA was better than that of the shale product but inferior to that of the perlite product. Both compressive strength and industry requirements were met or exceeded by the SLA product.
2. **Loose Fill Insulation.** Expanded perlite is used to fill the cavities in blocks used for construction of building exterior walls to improve their insulation properties. The property of interest defined by ASTM is the thermal resistance of the loose fill material. Thermal resistance requirements for perlite (7.4-11 lb/ft³) are 2.6-2.4 hr-ft²-°F/Btu. Tests using SLA with a unit weight of 29 lb/ft³ showed a thermal resistance of 1.46 hr-ft²-°F/Btu, which is somewhat lower than the values for perlite ULWAs. However, SLA has the advantage with respect to other industry requirements such as its free-flowing nature, low friability and hence low dustiness, and low moisture retention.
3. **Horticultural Applications.** SLA with a unit weight of <20 lb/ft³ was tested as a partial substitute for perlite and vermiculite at a commercial nursery. The control soil mix consisted of a combination of peat moss, bark, fiber, perlite, and vermiculite. Mixes were developed to

test the use of SLA as a substitute for perlite only, as well as for both perlite and vermiculite. The SLA proved to be a successful substitute for perlite alone but not for mixes calling for a mixture of perlite and vermiculite. The main problem with the SLA was its high drainage rate which necessitated more frequent watering. However, its higher unit weight was seen as an advantage in providing greater stability to larger potted plants and shrubs, and its higher strength was seen as an advantage in mechanized field/nursery applications.

4.3 Economics of SLA Production

The slag production economics were conducted using two parallel approaches:

- Comparison of the economics of SLA production vs. slag disposal
- Comparison of the economics of SLA production with the estimated market value of end products that can be made from it.

The market price of SLA was estimated taking into consideration the fact that it would likely command a lower price as a new, unproven material. The sale prices for SLA products were estimated at \$30/ton for block aggregates, \$35/ton for structural aggregates, and \$40/ton for roof tile and ultra-lightweight aggregate applications. Using a product mix based on the percentage of coarse and fine slag, the weighted average price of SLA was estimated at \$34.75/ton. This price was used to evaluate the economics of SLA production.

For purposes of this analysis, a value of \$15/ton is used as the cost of slag disposal, which is in the middle of the range of \$10-20/ton indicated for fly ash. Since these avoided costs would provide substantial savings to the gasifier operation, this amount could potentially be made available to the SLA production facility as a tipping fee per ton of slag accepted.

For the economic analysis, four scenarios were studied representing two sizes of IGCC facilities (200 MW and 400 MW) each using two methods of SLA production (rotary kiln and fluidized bed). For the rotary kiln processes, the SLA production costs were estimated at \$30.07/ton and \$24.40/ton for the 200 MW and 400 MW sizes respectively (220 and 440 tons/day capacity). Conventional LWA production costs were estimated at \$30.10/ton based on a survey of four operating plants.

The fluidized bed method of SLA production was found to be even more competitive because of lower capital and operating costs. Its production costs were \$26.48 and \$21.87 for the smaller and larger sizes respectively. Therefore, such systems should be considered for commercial SLA production, especially for lower-capacity plants. The economics for the larger-sized fluidized bed plant are especially attractive if the avoided costs of slag disposal are taken into account, as indicated by a payback period of under three years.

4.4 Recommendations for Future Work

IGCC technology is likely to play a major role in meeting the demand for energy in the United States, as well as in generation of syngas for chemical production. This assumption is substantiated by the rising prices of natural gas. As IGCC technology becomes a significant player in power generation, the technology for total utilization of the solid waste generated by the process (slag) should also be advanced. The development of slag utilization applications under this project has gone a long way toward meeting this goal. However, additional work is needed to test the durability of various SLA-based products and production techniques. The commercial adoption of SLA-based products would be accelerated by their recognition as acceptable aggregates by ASTM and other industry standards for applications in which they have been proven to meet applicable requirements.

Recently, there has been considerable interest in blending the coal feed to gasifiers with low-cost energy sources such as sewage sludge or refuse-derived fuel. These feed components will alter the basic chemistry of the slag produced. Systematic evaluation of slags produced from blended feeds would help to quantify how changing slag chemistry affects its expansion properties.

LIST OF ACRONYMS AND ABBREVIATIONS

ASTM	American Society for Testing and Materials
BWI	Bond Work Index, which represents the energy required for grinding
CMU	concrete masonry unit
DOE	U.S. Department of Energy
EPRI	Electric Power Research Institute
ICCI	Illinois Clean Coal Institute
IGCC	integrated-gasification combined cycle
LWA	lightweight aggregate
NCMA	National Concrete Masonry Association
NETL	National Energy Technology Laboratory
RCRA	Resource Conservation and Recovery Act
SLA	slag lightweight aggregate or expanded slag
SSD	saturated surface dry
TCLP	Toxicity Characterization Leaching Procedure
TEC	Tampa Electric Company
TGA	thermogravimetric analysis
ULWA	ultra-lightweight aggregate

Appendix A. Test Plan for Applications of Expanded Slags (Task 2.1)

1.0 Objectives

In Phase I, Praxis demonstrated its process for recovery of unconverted carbon (char) from slag. We also produced expanded lightweight aggregates ranging between 15-50 lb/ft³ unit weight from coal gasification slag at the pilot scale. In Phase II, the slag-based lightweight aggregates (SLA) will be characterized and tested for their suitability for various lightweight aggregate (LWA) and ultra-lightweight aggregate (ULWA) applications. This document outlines the testing procedure that will be followed during the evaluation process. This plan will also help potential users to identify the ways in which the expanded slag products differ from the conventional materials, and determine how best to modify the mix designs to utilize them while meeting the strength requirements specified by ASTM or industry standards.

SLA products will be characterized and tested for their suitability as substitutes for the following lightweight aggregate (LWA) applications:

- Structural concrete
- Concrete blocks
- Lightweight roof tiles
- Concrete panels.

SLA products will also be characterized and tested for their suitability as substitutes for the following ultra-lightweight aggregate (ULWA) applications:

- Insulating concrete
- Loose fill insulation
- Horticultural applications

The following other applications will also be tested:

- Pozzolanic material

ASTM Standard C 125 defines the term "coarse aggregate" as the aggregates that are predominantly retained on a 4-mesh (4.75-mm) sieve. The term "fine aggregate" applies to aggregates that almost entirely pass a 4-mesh sieve but are predominantly retained on a 200-mesh (0.074-mm) sieve. Another commonly used term is "combined aggregate," which represents a mixture of coarse and fine aggregates. Various potential applications for which specific expanded SLA products that may be evaluated are identified in Table A-1 and the test needs and procedures are outlined in various sections in this document.

Table A-1: Application Tests and Associated Expanded Slag Samples to be Used

	Aggregates Targeted for Substitution	Expanded Slag Product Sample		Ref. Section	
LWA Applications					
	Target Size/Specifications	Unit Wt	Expanded Slag	Slag/Clay Pellets ⁽¹⁾	
Structural concrete	(i) 3/4" coarse LWA ASTM C330	50 lb/ft ³	-----	50/50	2.1.1
	(ii) 3/8" combined LWA ASTM C330	50 lb/ft ³	1/4" x 50M	-----	2.1.2
	(iii) 3/4" pilot plant LWA	50 lb/ft ³	-----	0/100	2.1.3
CMU concrete	Fine (-4M) LWA	50 lb/ft ³	1/4" x 50M	50/50	
Roof tile concrete	Two SLA samples of fine (-6M) LWA, size gradation given by manufacturer and two control samples	40 lb/ft ³	Crushed 1/4" x 50M	50/50 (Crushed)	
ULWA Applications					
Insulating concrete	ASTM C332 Group II (45-90 lb/ft ³ concrete)			---	
Loose fill insulation	ASTM C549	<12 lb/ft ³	10 x 50M	---	
Horticulture	Expanded perlite size range	<12 lb/ft ³	10 x 50M	---	
Other Applications					
Pozzolanic material	ASTM C311	30 lb/ft ³	10 x 50M	---	

2.0. Testing of SLA for Structural Lightweight Concrete Applications

The objective of this test program will be to develop mix designs using expanded slag lightweight aggregates (SLA) to produce sand-lightweight aggregate-based cement concrete of 2500-4000 psi strength with corresponding unit weights ranging between 115-105 lb/ft³ by varying the cement content in the mix. Samples of SLA to be tested are identified in Table A-2. In addition, a sample of a commercially available structural aggregate will be tested as a control sample during the testing of materials identified under items (i) and (ii) in the table. As may be seen in the table, testing of SLA as 3/4" coarse aggregates will involve demonstration of three levels of strength (complete matrix), whereas testing with the other samples will only involve one level of cement.

Table A-2: SLA Products to be Tested and Tentative Cement Levels

SLA Products to be Tested	Tentative Level of Cement, Sacks/Yard ³
(i) 3/4" expanded SLA (50/50 slag-clay pellets) as 3/4" coarse LWA	5½, 6½ and 7½
(ii) 1/4" x 50M expanded SLA crushed as 3/8" combined LWA	One level of cement
(iii) Expanded 3/4" clay pellets produced during the pilot program	One level of cement

Exploratory testing may be necessary to establish the appropriate sand, water or cement requirements and confirm the strength and unit weight of the resulting concrete prior to completing the final batch of tests.

The ASTM unit weight requirements for the structural concrete aggregates are summarized in Table A-3. Also provided in Table A-3 are the unit weight and compressive strength requirements for cement concrete mixtures produced from 100% LWA or various mixtures of LWA and sand for reference purposes.

Table A-3: Lightweight Aggregate and Structural Concrete Unit Weight and Compressive Strength Requirements (ASTM C 330)

Structural Lightweight Aggregate Unit Weight Requirements			
	Fine Aggregate	Coarse Aggregate	Combined
	lb/ft³ (kg/m³)	lb/ft³ (kg/m³)	lb/ft³ (kg/m³)
Unit weight, maximum values	70 (1120)	55 (880)	65 (1040)
Lightweight Structural Concrete Unit Weight and Strength Requirements			
Concrete Unit Weight		28-Day Compressive Strength	
lb/ft³	(kg/m³)	lb/in²	MPa
All Lightweight Aggregate			
110	(1760)	4000	(28)
105	(1680)	3000	(21)
100	(1600)	2500	(17)
Sand-Lightweight Aggregate			
115	(1840)	4000	(28)
110	(1760)	3000	(21)
105	(1680)	2500	(17)

2.1 Procedure for Evaluation of Pelletized (50/50) SLA as 3/4" Coarse Aggregates

The following procedure will be used for preparation of aggregate:

- Obtain a sample of commercially available 3/4" coarse structural LWA for use as a control. Measure its unit weight and conduct a sieve analysis. (This sample will be provided by Praxis.)
- Crush 25 lb 50/50 slag/clay blend extruded for pelletization, and expanded to 50 lb/ft³ unit weight to pass 1" top size in order to meet the ASTM C 330 for 3/4" coarse aggregates. Compare the size distribution of this material with that of the commercial LWA sample. (This sample will be prepared and supplied by Fuller Co.)

The following procedure will be used for preparation of cement concrete:

- Saturate all the aggregates overnight to bring them to the saturated surface dry (SSD) condition and document their moisture content.
- Estimate the sand content for the concrete mix to achieve a suitable gradation in the mix.
- Prepare cement concrete mixes using the slag aggregates prepared above. Use an aggregate-to-cement ratio identified by exploratory test to achieve a 28-day strength of 2500, 3000, and 4000 psi respectively. Document the water required and calculate the

cement-to-water ratio. Also, report the final volume and weight of the ingredients used in the mix design and measure the unit weight of the concrete. Prepare sufficient test specimens for the following tests (estimated at 12-15).

- Conduct 3-day, 7-day, and 28-day compressive strength tests as per ASTM and use the average of 3 measurements.
- Save test specimens to conduct the following tests if decided at a later date:
 - Conduct Freeze Thaw as per C 666
 - Conduct Drying Shrinkage as per C157
 - Conduct Staining C 641.
- Prepare control test specimens using the commercial LWA sample with an identical aggregate-to-cement ratio and slump for the 3000 strength. Measure the water added to document the cement-to-water ratio. Measure the unit weight of the concrete and compressive strengths for 3-day, 7-day and 28-day curing time for comparison.

2.2 Procedure for Evaluation of SLA as 3/8" Combined Aggregates

Tests will be conducted using 1/4" x 50M SLA to evaluate it as 3/8" combined LWA which is 100% passing 1/2" top size. The unit weight of the expanded slag is to be chosen such that the finished concrete is within 110 lb/ft³. A sample of commercially available 3/8" combined structural LWA will be used to prepare a control mix and to compare its gradation with the prepared 1/4" x 50M SLA. The sand content for the concrete mix will be estimated to achieve a suitable gradation for this application.

The following procedure will be used for preparation of aggregates:

- Procure a 3/8" combined commercially available LWA for use as a control. Conduct a sieve analysis for use as a guideline for preparing the expanded slag. (This sample will be provided by Praxis.)
- Prepare 10 lb of SLA to meet ASTM 330 3/8" combined aggregate size requirements using 50 lb/ft³ expanded 1/4" x 50M slag (or by blending appropriate quantities of 1/4" x 10M and 10M x 50M SLA fractions). Crush this material to pass 1/2" top size and screen out any excess fines. Run a sieve analysis of the final crushed expanded slag aggregates and compare these with the commercially available 3/8" combined aggregate. (This sample will be prepared and supplied by Fuller Co.)

The following procedure will be used for preparation of cement concrete:

- Saturate all the aggregates overnight to bring them to the saturated surface dry (SSD) conditions and document their moisture content
- Estimate the sand content for the concrete mix to achieve a suitable gradation in the mix.

- Prepare cement concrete mixes using the slag aggregates prepared above. Use an aggregate-to-cement ratio identified by exploratory testing to achieve a 28-day strength of 3000 psi. Document the water required and calculate the cement-to-water and aggregate-to-sand ratios. Also, report the final volume and weight of the ingredients used in the mix design and measure the unit weight of the concrete. Prepare sufficient test specimens for the tests listed below.
- Measure the unit weight of the concrete and conduct 3-day, 7-day, and 28-day compressive strength tests as per ASTM, using the average of 3 measurements. Save samples for freeze/thaw tests.
- Prepare control test specimens using the commercial LWA sample with an identical aggregate-to-cement ratio and slump. Measure the water added to document the cement-to-water ratio. Measure the unit weight of the concrete and compressive strength for 3-day, 7-day and 28-day curing time for comparison.

2.3 Procedure for Evaluation of Pelletized Clay as 3/4" Coarse Aggregates

The purpose of this testing is to compare the performance of the control sample of expanded LWA produced from extruded clay pellets produced during pilot kiln operations.

The following procedure will be used for preparation of aggregates:

- Procure a sample of commercially available 3/4" coarse structural LWA for use as a control. Measure its unit weight and conduct a sieve analysis. (This sample will be supplied by Praxis.)
- Crush 10 lb of extruded clay pellets expanded to 50 lb/ft³ unit weight to pass 1" top size in order to meet the ASTM C 330 for 3/4" coarse aggregates. Compare the size distribution of this material with that of the commercial LWA sample. (This sample will be prepared and supplied by Fuller Co.)

The following procedure will be used for preparation of cement concrete:

- Saturate all the aggregates overnight to bring them to saturated surface dry (SSD) conditions and document their moisture content
- Estimate the sand content for the concrete mix to achieve a suitable gradation in the mix.
- Prepare cement concrete mixes using the clay pellet aggregates prepared above. Use an aggregate-to-cement ratio to achieve a 28-day strength of 3000 psi. Target a slump identical to the other tests, document the water required, and calculate the cement-to-water and aggregate-to-cement ratios. Also, report the final volume and weight of the ingredients used in the mix design.

- Measure the unit weight of the concrete and conduct 3-day, 7-day, and 28-day compressive strength tests as per ASTM and using the average of three measurements.

2.4 Data and Reports

Provide laboratory data sheets with brief comments on the nature of the results.

3.0. ROOF TILE CONCRETE APPLICATION TESTING

The objective of this testing is to confirm if the (i) expanded slag, (ii) pelletized slag and (iii) pelletized clay aggregates can meet roof tile aggregate requirements. Lightweight concrete roof tiles are made with LWA and a high cement paste, which is molded continuously. The paste also contains a plasticizer and an accelerator. Each manufacturer use a proprietary mix design. Curing is done in a high-temperature, high-humidity atmosphere for the initial 4 hours. The remainder of the curing is done on shrink-wrapped pallets in the yard. Aggregates used for roof tile application are typically fine aggregates as per ASTM C 331 (85-100% passing 4 mesh). However, roof tile manufacturers also specify particle size distribution along with a unit weight of 40 lb/ft³. This application is very demanding due to the high compressive strength and flexural strength requirements. The typical 28-day compressive strength of the concrete is over 5,000 psi at unit weight of 108 lb/ft³.

3.1. Procedure for Evaluation of SLA 50/50 pellets (35-40 lb/ft³)

The first step is to prepare the manufacturer specified size gradation by stage crushing and screening. The target unit weight of the aggregates is 40 lb/ft³. The following procedure will be used for aggregate preparation:

- Procure a 50-lb sample of roof tile aggregate from a roof tile manufacturer for use as a control sample. Conduct moisture analysis and screen analysis, and measure the fractional unit weights.
- Crush 50:50 expanded slag/clay pellets with a unit weight of 35-40 lb/ft³ to pass a minus-4M sieve in stages to reproduce the size distribution as per the range provided by the roof tile manufacturer. Conduct the following tests and compare the results with the manufacturer's specifications and with the conventional aggregate sample as appropriate:
 - Moisture absorption (target <15% by wt.)
 - Sieve analysis at 4, 8, 16, 30, 50, and 200M sieves
 - Unit weight by size fractions and for the whole sample.
- Crush the expanded all clay pellets of 35-40 lb/ft³ unit weight to pass -4M sieve following the procedure given above. Conduct the following tests and compare the results with the manufacturer's specifications and with the conventional aggregate sample as appropriate:

- Moisture absorption (target <15% by wt.)
- Sieve analysis at 4, 8, 16, 30, 50, and 200M sieves
- Unit weight by size fractions and for the whole sample

The following procedure will be used for preparation of cement concrete:

- Saturate all the aggregates overnight to bring them to saturated surface dry (SSD) conditions and document their moisture content
- Prepare a batch of cement concrete sufficient to make test specimens using the mix design given below. Mix the ingredients thoroughly using a mechanical mixer or by hand, keeping track of the mixing time for preparing subsequent batches. Additives may be used based on the manufacturer's recommendation, as given below:
 - Cement-to-aggregate ratio by weight: 1:2.5 on dry basis
 - Cement type: Type II
 - Accelerator (HICO HB98): 3.5 ml/100 g of cement
 - Plasticizer (MBL Rheobuilt): 3.5 ml/100 g of cement
 - Slump: 0-1
- Prepare 15 2" specimens using the above mix design taking care to avoid the formation of air voids. The test specimens are to be cured in a chamber at 120°F and 95% RH for 4 hours. Subsequent curing will be done in a constant-temperature bath as per ASTM.
- Document the total weight and volume of ingredients used and calculate the water-to-cement ratio. Measure the unit weight of the fresh concrete. Report the workability of the mix.
- Test the specimens for compression following 1-day (early strength), 3-day, 7-day, and 28-day curing times. Save three cylinders for further testing.

3.2. Procedure for Evaluation of SLA (35-40 lb/ft³) as Roof Tile Aggregates

The first step is to prepare the manufacturer's specified size gradation by stage crushing and screening. The target unit weight of the aggregates is 40 lb/ft³. The following procedure will be used for preparation of aggregates:

- Stage crush 10 x 50M SLA with a unit weight of 35-40 lb/ft³ to pass a minus-4M sieve in stages to reproduce the size distribution as per the range provided by the roof tile manufacturer. Conduct the following tests and compare the results with the manufacturer's specifications and with the conventional aggregate sample as appropriate:
 - Moisture absorption (target <15% by wt.)
 - Sieve analysis at 4, 8, 16, 30, 50, and 200M sieves
 - Unit weight by size fractions and for the whole sample

The following procedure will be used for preparation of cement concrete:

- Adjust the moisture content of the aggregates to SSD conditions.
- Prepare a batch of cement concrete sufficient to make test specimens using the mix design given below. Additives may be used based on the manufacturer's recommendation. Mix the ingredients thoroughly using a mechanical mixer or by hand, keeping track of the mixing time for preparing subsequent batches.
 - Cement-to-aggregate ratio by weight: 1:2.5 on dry basis
 - Cement type: Type II
 - Accelerator (HICO HB98): 3.5 ml/100 g of cement
 - Plasticizer (MBL Rheobuilt): 3.5 ml/100 g of cement
 - Slump: 0-1
- Prepare 15 2" specimens using the above mix design taking care to avoid the formation of air voids. The test specimens are to be cured in a chamber at 120°F and 95% RH for 4 hours. Subsequent curing will be done in a constant-temperature bath as per ASTM.
- Document the total weight and volume of the ingredients used and calculate the water-to-cement ratio. Measure the unit weight of the fresh concrete. Report the workability of the mix.
- Test the specimens for compression following 1-day (early strength), 3-day, 7-day, and 28-day curing times. Save 3 cylinders for further testing.

3.3 Procedure for Testing Expanded Clay (35-40 lb/ft³)

The following aggregate preparation method will be used:

- Repeat the steps for size reduction given above for crushing 50/50 pellets
- Conduct the following tests and compare the results with the manufacturer's specifications and with the conventional aggregate sample as appropriate:
 - Moisture absorption (target <15% by wt.)
 - Sieve analysis at 4, 8, 16, 30, 50, and 200M sieves
 - Unit weight by size fractions and for the whole sample

The following procedure will be used for preparation of cement concrete:

- Prepare a concrete mix design using the procedure given above.
- Prepare 12 2" cylinders to conduct early (1-day), 3-day, 7-day and 28-day strength tests.

4.0. LIGHTWEIGHT BLOCK AGGREGATE SPECIFICATIONS

ASTM C 331 specifies unit weight requirements for aggregates and unit weight and strength requirements for cement concrete used in manufacturing lightweight concrete masonry units. These requirements are summarized in Table A-4.

Table A-4: LWA and Cement Concrete Requirements for CMU Applications

Lightweight Aggregate Unit Weight Requirements for CMU (ASTM C 331)				
		Fine lb/ft ³ (kg/m ³)	Coarse lb/ft ³ (kg/m ³)	Combined lb/ft ³ (kg/m ³)
Unit weight, max. values		70 (1120)	55 (880)	65 (1040)
Industry preference		NA	NA	50 (800)
Lightweight Concrete Unit Weight and Strength Requirements for CMU				
			28-Day Compressive Strength	
	ASTM	Unit Weight lb/ft ³ (kg/m ³)	Gross psi (MPa)	Net psi (MPa)
Load-bearing				
- below grade	C 90	<105 (1682)	1000 (14)	2000 (28)*
- above grade	C 90	<85 (1362)	700 (10)	1400 (20)*
Nonload-bearing	C 129	105 (1682)	NA	600 (8.4)

*Net compressive strength values calculated by assuming net cross-sectional area is 50% of gross area.

As would be expected, the strength requirements for load-bearing blocks are higher than those for nonload-bearing units. The standard does not, however, specify the cement concrete mix design for blocks, thus allowing a degree of flexibility.

5.0 CONCRETE PANELS

This work will be done using the laboratory of a leading manufacturer of cement concrete panels. The will use their internal procedure for evaluation of the SLA in this application.

6.0 INSULATING CONCRETE

Perlite insulating concrete is made from perlite (a Group I aggregate), portland cement, water, and other additives including an air-entraining agent. Insulating concrete made with perlite has an oven-dry unit weight of 15-50 lb/ft³. Insulating concrete may also be made from expanded shale, blast-furnace slag, or fly ash (Group II aggregates), resulting in a concrete unit weight of 50-90 lb/ft³. The minimum compressive strength for perlite insulating concrete recommended by the Perlite Institute is 350 psi at a concrete unit weight of 36 lb/ft³, and 80 psi at a concrete unit weight of 22 lb/ft³.

6.1 Procedure for Preparation Of SLA For Use In Insulating Concrete

ASTM C 332 provides specifications for insulating concrete aggregates. The detailed specifications for perlite and vermiculite aggregates (Group I) and shale-based aggregates (Group II) for insulating concrete are given in ASTM C 332 and summarized in Table A-5. The category selected for testing of SLA is Combined (Fine and Coarse) 3/8" x 0 Aggregates. The material used for these tests would be an appropriate mix of 1/4" x 10 mesh, 10 x 50 mesh expanded slag and necessary portions of pulverized expanded slag to replicate the ASTM C 332 (Table A-5) size requirements. A 70-lb batch of aggregate will be prepared for this purpose. Aggregate sample preparation will be done at Fuller and the preparation of test specimens and compression testing will be done at Penn State. The thermal conductivity specimen will be shipped to Energy Materials Testing Laboratory in Biddeford, Maine.

Table A-5: Aggregate Specifications for Insulating Concrete (ASTM C332)

Aggregate Size and Unit Weight						
	Size		Minimum		Maximum	
	Mesh/inch	(mm)	Unit Weight, lb/ft ³ (kg/m ³)			
Group I Aggregates (Perlite and Vermiculite)						
Perlite	-4 M	(4.75)	7.5	(120)	12	(196)
Vermiculite (coarse)	-3/8"	(9.5)	5.5	(88)	10	(160)
Vermiculite (fine)	-8 M	(2.36)	5.5	(88)	10	(160)
Group II Aggregates (Shale, Ash, and Blast Furnace Slag)						
Fine	4 M x 0	(4.75 x 0)	--		70	(120)
Coarse	1/2" x 4 M	(12.5 x4.75)	--		55	(880)
Coarse	1/8" x 8 M	(9.5 x 2.36)	--		55	(880)
Coarse	4 x 8 M	(4.75 x2.36)	--		55	(880)
Combined	1/2" x 0	(12.5 x 0)	--		65	(1040)
Combined	3/8" x 0	(9.5 x 0)	--		65	(1040)
Unit Weight and Thermal Conductivity of Insulating Concrete						
	Unit Weight		Thermal Conductivity			
	lb/ft ³	(kg/m ³)	Btu-in./h-ft ² -° F		(W/m-K)	
Group I Aggregates (perlite-based)	15-50	(240-800)	0.45-1.5		(0.065-0.22)	
Group II Aggregates (shale-based)	50-90	(800-1440)	1.5-3.0		(0.22-0.43)	

6.2 Preparation Of SLA-Based Concrete For Use In Insulating Concrete

The Perlite Institute has provided typical mix proportions for perlite insulating concrete. The mix design calls for using appropriate quantities of polypropylene fiber (15 denier, 1/4" to 1/2" long) and an air-entraining agent. These tests are to be done using a cement-to-concrete ratio of 1:5 by volume. However, if the addition of fiber becomes a problem, a cement-to-aggregate ratio of 1:6 is to be used without fiber. This will allow direct comparison of the results with the Perlite Institute data. The following test specimens are to be prepared:

- 2" cubes for unit weight, and 7-day and 28-day compression testing
- 12 inch square and 1" thick specimens for thermal conductivity testing.

7.0 LOOSE FILL INSULATION MATERIALS

Expanded perlite is used to enhance the insulating properties of walls by filling the voids in masonry blocks. Typically, minus 4-mesh expanded perlite, with a 2-11 lb/ft³ unit weight, is surface-treated with silicone to improve its water repellency prior to use in this application. Other material characteristics that are important for this application include high thermal resistance and low combustibility.

7.1 Preparation Of SLA For Use In Loose Fill Insulation

ASTM C 459 provides specifications for loose fill insulation aggregates. The detailed specifications for expanded perlite used for loose fill insulation are given in ASTM C 549, which are summarized in Table A-6. A 10-lb batch of aggregate will be prepared (by screening) from SLA of the lowest unit weight produced from the fluid bed expander. Aggregate sample preparation and its characterization testing (unit weight, water repellency testing) will be done at Fuller. The sample will be shipped to Penn State for shipment Energy Materials Testing Laboratory in Biddeford, Maine, along with the insulating concrete specimens for thermal conductivity testing.

Table A-6: Perlite-Based Loose Fill Insulation Specifications (ASTM C 549)

Physical Specifications			
	Type I-II		Type III-IV
Unit weight, lb/ft ³ (kg/m ³)	2-11 (32-176)		2-11 (32-176)
Maximum +4 mesh (4.75 mm)	5%		5%
Water repellency (min. ml H ₂ O repelled)	NA		175
Moisture absorption (max. wt%/14 days)	1.0%		1.0%
Wickability (max. grams wicked in 5 minutes)	NA		1.0
Combustibility (E 136)	None		NA
Dust suppression (max. wt of collected material, mg)	NA		85
Thermal Resistance for 1-in. (25.4 mm) Thickness at Various Temperatures			
Unit weight	Thermal resistance, h-ft ² -°F/Btu (m ² -k/W)		
lb/ft ³ (kg/m ³)	At 4°C	At 24°C	At 41°C
2.0-4.1 (32.0-65.5)	4.3-3.9 (0.78-0.69)	3.9-3.3 (0.65-0.58)	3.7-3.2 (0.65-0.56)
4.1-7.4 (65.6-118.4)	3.9-3.3 (0.69-0.58)	3.3-2.8 (0.58-0.49)	3.2-2.7 (0.56-0.47)
7.4-11.0 (118.4-176.0)	3.3-2.9 (0.58-0.51)	2.8-2.4 (0.49-0.42)	2.7-2.4 (0.47-0.42)

Type I: Expanded products
 Type II: Surface treated for H₂O repellency
 Type III: Surface treated for dust control
 Type IV: Surface treated for H₂O repellency and dust control.

8.0 HORTICULTURAL APPLICATIONS

SLA will be tested as a partial replacement for expanded perlite and vermiculite in horticultural applications. The specialized nature of this work requires that it be done with the involvement of a nursery. Procedures followed in evaluating conventional materials will be used to evaluate the expanded slag.

Sulfur Market Data

Sulfur

PRODUCER	CAPACITY*
AtoFina Petrochemicals (2 locations)	135
BP (18 locations)	1,375
ChevronTexaco (8 locations)	1,190
CITGO Petroleum (3 locations)	370
ConocoPhillips (11 locations)	485
Delhi Gas Pipeline (4 locations)	120
Dow, Freeport, Tex.	150
Dynergy Midstream Services (5 locations)	285
El Paso Refining and Chemical	100
ExxonMobil (13 locations)	2,110
Jupiter Sulfur (3 locations)	145
Koch Industries (ten locations)	400
Lyondell-Citgo, Houston, Tex.	320
Marathon Ashland Petroleum (8 locations)	390
Motiva Enterprises (4 locations)	780
Premcor (2 locations)	175
Pursue Energy, Thomasville, Miss.	580
Republic Refining, Puckett, Miss.	185
Shell (13 locations)	1,065
Sunoco (2 locations)	115
Tosco (4 locatons)	275
Trident NGL (2 locations)	240
Valero Energy (9 locations)	440
Vintage Petroleum (2 locations)	115
Western Gas, (3 locations)	160
Others**	420
Total	12,125

*Thousands of long tons per year of elemental sulfur, excluding values produced or reclaimed in the form of sulfuric acid, hydrogen sulfide, or pyrites. Elemental sulfur is recovered from oil refinery acid gas streams, containing H₂S and SO₂, and natural gas production, where H₂S is removed from the raw gas.

**Companies whose refinery or natural gas recovery sulfur capacity totals less than 100,000 long tons per year.

In 2003, IMC Global Inc. acquired the sulfur transportation, marketing and distribution assets of Freeport-McMoRan Sulphur, a subsidiary of McMoRan Exploration Co., which exited the sulfur business. The acquisition was made through a new 50-50 joint venture with Savage Industries Inc., to be known as Gulf Sulphur Services Ltd. In 2000, Freeport McMoRan closed its last mine employing the Frasch method of producing sulfur, at Main Pass, La. Reduced demand, low sulfur pricing and high production costs were the driving forces that closed the mine with more than 2 million tons per year of capacity.

Exxon and Mobil merged in 1999 to form the new entity, ExxonMobil. ARCO (Atlantic Richfield Company) was acquired in 2000 by BP Amoco. A new unified global brand, centered on the name BP was subsequently adopted. Fina Oil and Chemical Company is now AtoFina Petrochemicals, a subsidiary of AtoFina, which was formed in 2000 by the merger of Elf Atochem with TotalFina.

Equilon Enterprises is the joint venture that was formed in 1998 by Shell Oil and Texaco. In October 2001, Chevron Corp. and Texaco Inc. merged, forming ChevronTexaco Corp. As part of the merger, Texaco sold its stakes in Equilon Enterprises and Motiva Enterprises to Shell Oil Company and Saudi Refining, with Shell becoming the sole owner of Equilon, and Shell and Saudi Refining jointly owning Motiva. As of March 2002, Equilon Enterprises was renamed Shell Oil Products US. In 2000, Tosco Corp. purchased the Wood River, Ill., Equilon Enterprises refinery from Shell Oil and Texaco. In September 2001, Phillips Petroleum Company finalized its acquisition of Tosco. In August 2002, Phillips Petroleum Company and Conoco Inc. merged to form ConocoPhillips.

DEMAND

2000: 12,730 thousand long tons; 2001: 10,650 thousand long tons; 2005: 11,530 thousand long tons, projected. Demand equals production plus imports (2000: 970 thousand long tons; 2001: 550 thousand long tons) less exports (2000: 690 thousand long tons; 2001: 465 thousand long tons).

GROWTH

Historical (1996 - 2001): -5.1 (negative) percent per year; future: 2.0 percent per year through 2005.

PRICE

Historical (1996 - 2001): high \$77.00 per long ton, contract, del.; Tampa, Fla.; low, \$25.00 per long ton, same basis. Current: \$58.00 per long ton, same basis.

USES

Sulfuric acid (primarily for fertilizer manufacture) 96 percent; other uses including production of carbon disulfide, sulfur dioxide and phosphorous pentasulfide; pulp and paper uses; and rubber vulcanizing, 4 percent.

STRENGTH

While demand has improved modestly this year, the supply-side has been constrained, particularly during the second half of this year. The tightening market is chiefly the result of increased fertilizer operating rates and the curtailment of Canadian smelter capacity, which reduced the production of smelter sulfuric acid. This shortfall called for more elemental sulfur to produce virgin sulfuric acid. The tight market has increased sulfur pricing significantly.

WEAKNESS

In the early 1990s, sulfur prices were more than \$100 per long ton but have been below \$80 per long ton since 1993 due to excess sulfur supplies. Significantly decreased production in the domestic phosphate fertilizer industry, resulted in dramatically lower sulfur consumption and

correspondingly lower prices last year. Sulfur prices fell to below \$30 per long ton for a short period in mid-2001 due to excess supplies as phosphoric acid production was reduced.

OUTLOOK

Increased production of phosphate fertilizers has stimulated demand for sulfur, but most of this increase is being met with additional imported product as world supplies remain in surplus. This trend in both demand and supply is expected to carry forward. Production of recovered elemental sulfur from petroleum refineries will continue its steady growth, supported by new facilities being installed to increase refining capacity and the capability of current operations to handle higher sulfur crude oil.

Additional equipment will be installed at many refineries to reduce the sulfur in gasoline and diesel fuel to comply with the new environmental regulations going into effect, which limit the sulfur content of gasoline and diesel fuel. Demand growth over the forecast period is anticipated to be 2 percent annually.

U.S. Geological Survey Information on the Sulfur Market

U.S. Geological Survey
Information On Sulfur Market

SULFUR

By Joyce A. Ober

Domestic survey data and tables were prepared by Brian W. Jaskula, statistical assistant, and the world production table was prepared by Glenn J. Wallace, international data coordinator.

Recovered sulfur production reached an alltime high of 9.4 million metric tons (Mt), with a 6.0% increase from oil refineries, and a slight increase of sulfur production at natural gas processing operations. Even byproduct sulfuric acid production from nonferrous metal smelters, which had been in decline since 2001, increased by 8.2% to reach 739,000 metric tons (t) of contained sulfur. Exports, imports, and consumption increased; producers' stocks decreased.

The United States was once again the world's leading sulfur producer in 2004 with total production of 10.1 Mt of sulfur in all forms. All elemental sulfur and byproduct sulfuric acid was produced as a result of efforts to meet environmental requirements that limit atmospheric emissions of sulfur dioxide. Worldwide, environmental regulations contributed to increased sulfur recovery, and strong worldwide demand slowed the decline in production of native sulfur to about 4.2%, which had been in steep decline since 2000. In the few countries where pyrites remain an important raw material for sulfuric acid production, the sulfur content of pyrites production increased by 5.9%.

Expanded production continued to outpace sulfur demand growth, which resulted in increased stocks at some operations, especially at a few in remote locations from which it is difficult and costly to ship the product to market. Some remelting at more market-accessible stockpiles occurred to meet global demand.

Through its major derivative, sulfuric acid, sulfur ranks as one of the most important elements used as an industrial raw material and is of prime importance to every sector of the world's fertilizer and manufacturing industries. Sulfuric acid production is the major end use for sulfur, and consumption of sulfuric acid has been regarded as one of the best indices of a nation's industrial development. More sulfuric acid is produced in the United States every year than any other inorganic chemical; 37.5 Mt, which is equivalent to about 12.3 Mt of elemental sulfur, was produced in 2004, slightly more than that of 2003 (U.S. Census Bureau, 2005).

In 2004, nearly all salient U.S. sulfur statistics were higher than the corresponding values in 2003. Domestic production and shipments of sulfur in all forms were 5.4% and 5.7% higher, respectively, than those of 2003. Consumption increased, and exports, imports, prices, and values were higher (table 1; figures 1-4). Only stocks were down in 2004.

Estimated world sulfur production was more than 3.5% higher in 2004 than it was in 2003 (table 1). Recovered elemental sulfur is produced primarily during the processing of natural gas and crude petroleum. For the fourth consecutive year, more than 90% of the world's sulfur production came from recovered sources. Some sources of byproduct sulfur are unspecified, which means that the material could be elemental or byproduct sulfuric acid. The quantity of sulfur produced from recovered sources was dependent on the world demand for fuels, nonferrous metals, and petroleum products, rather than for sulfur.

World sulfur consumption was slightly higher than it was in 2003; about 50% was used in fertilizer production, and the remainder, in myriad other industrial uses. World trade of elemental sulfur increased by 9.3% from the levels recorded in 2003. Worldwide inventories of elemental sulfur were relatively unchanged.

Legislation and Government Programs

The U.S. Environmental Protection Agency (EPA) issued the final rule on the sulfur content for nonroad diesel on May 11. This regulation reduced the allowable sulfur level in fuel used in farm and construction equipment to 500 parts per million (ppm) by 2007 and 15 ppm by 2010, from a current limit of 3,000 ppm. The new standards are the same as the requirements for on-road diesel except for the time for implementation. Highway diesel must meet the lower limit by mid-2006. The EPA was working on a similar proposal for diesel burned in marine and locomotive engines (Lorenzetti, 2004).

Production

Elemental Sulfur.—U.S. production statistics were collected on a monthly basis and published in the U.S. Geological Survey (USGS) monthly sulfur Mineral Industry Surveys. All of the 110 operations to which survey requests were sent responded; this represented 100% of the total production listed in table 1. In 2004, production and shipments were about 5.1% and 5.6% higher than those of 2003. The value of shipments was 19.5% higher than in 2003 owing to an increased average unit value of elemental sulfur. Trends in sulfur production are shown in figures 1 and 3.

Frasch.—Until 2000, native sulfur associated with the caprock of salt domes and in sedimentary deposits in the United States was mined by the Frasch hot-water method in which the native sulfur was melted underground with super-heated water and brought to the surface by compressed air. Freeport-McMoRan Sulphur Inc. (a subsidiary of McMoRan Exploration Co.) closed the last domestic Frasch mine, Main Pass, in 2000 (Fertilizer Markets, 2000).

Recovered.—Recovered elemental sulfur, which is a nondiscretionary byproduct from petroleum-refining, natural-gas-processing, and coking plants, was produced primarily to comply with environmental regulations that were applicable directly to emissions from the processing facility or indirectly by restricting the sulfur content of the fuels sold or used by the facility. Capacity utilization at U.S. refineries was about 96% during the year (North American Sulphur Review, 2004d). Recovered sulfur was produced by 38

companies at 109 plants in 26 States and 1 plant in the U.S. Virgin Islands. Most of these plants were small with only 36 reporting production that exceeded 100,000 metric tons per year (t/yr). By source, 78.8% of recovered elemental sulfur production came from petroleum refineries or satellite plants that treated refinery gases and coking plants, and the remainder was produced at natural-gas treatment plants (table 3).

The leading producers of recovered sulfur, all with more than 500,000 t of sulfur production, in descending order of production, were Exxon Mobil Corp., BP p.l.c., ConocoPhillips Co., Chevron Corp., Valero Energy Corp., Shell Oil Co. (including its joint-ventures with Petróleos Mexicanos, S.A. de C.V. and Saudi Refining Inc. and subsidiary operations), CITGO Petroleum Corp. (including its joint-venture refinery it owns with Lyondell Chemical Co.), and Burlington Resources Inc. The 65 plants owned by these companies accounted for 78.6% of recovered sulfur output during the year. Recovered sulfur production by State and district is listed in tables 2 and 3.

Four of the world's 17 largest refineries, each with a crude processing capacity of nearly 450,000 billion barrels per day or more, are in the United States. They are, in decreasing order of production, ExxonMobil's Baytown, TX, refinery; Hovensa LLC's St. Croix, VI, refinery; ExxonMobil's Baton Rouge, LA, refinery; and BP's Texas City, TX, refinery (Nakamura, 2004). The capacity to process large quantities of crude oil does not necessarily mean that refineries recover large quantities of sulfur, but all of these refineries were major producers of refinery sulfur. Sulfur production depends on installed sulfur recovery capacity as well as the types of crude oil that are refined at the specific refineries. Major refineries that process low-sulfur crudes may have relatively low sulfur production.

U.S. refineries were installing equipment to meet the lower sulfur limits on finished fuels that took effect in 2004 and others that will take effect in 2006. Expensive processes were necessary to meet these requirements, but several refiners were also installing additional equipment to enable refineries to process heavy, sour crudes, especially those from Canada, Mexico, and Venezuela (North American Sulfur Review, 2004h).

Byproduct Sulfuric Acid.—Sulfuric acid production at copper, lead, molybdenum, and zinc roasters and smelters accounted for about 7.3% of the total domestic production of sulfur in all forms and totaled 739,000 t; this was an increase of 8.2% compared with that of 2003 (table 4). Three acid plants operated in conjunction with copper smelters, and three were accessories to lead, molybdenum, and zinc smelting and roasting operations. The three largest sulfuric acid plants were associated with copper mines and accounted for 81.2% of the output. The copper producers—ASARCO Incorporated, Kennecott Utah Copper Corp., and Phelps Dodge Corp.—each operated a sulfuric acid plant at their primary copper smelters.

Consumption

Apparent domestic consumption of sulfur in all forms was 7.7% higher than that of 2003 (table 5). Of the sulfur consumed, 71.5% was obtained from domestic sources—elemental sulfur (66.3%) and byproduct acid (5.3%)—compared with 73.5% in 2003 and 74.6% in 2002. The remaining 28.5% was supplied by imports of recovered elemental sulfur (22.3%) and sulfuric acid (6.1%). The USGS collected end-use data on sulfur and sulfuric acid according to the standard industrial classification of industrial activities (table 6).

Sulfur differs from most other major mineral commodities in that its primary use is as a chemical reagent rather than as a component of a finished product. This use generally requires that it be converted to an intermediate chemical product prior to its initial use by industry. The leading sulfur end use, sulfuric acid, represented 59.1% of reported consumption with an identified end use, and it is reasonable to assume that nearly all of the sulfur consumption reportedly used in petroleum refining was first converted to sulfuric acid, bringing sulfur used in sulfuric acid to 86.8% of the total. Some identified sulfur end uses were tabulated in the "Unidentified" category because these data were proprietary. Data collected from companies that did not identify shipment by end use also were tabulated as "Unidentified." A significant portion of the sulfur in the "Unidentified" category may have been shipped to sulfuric acid producers or exported, although data to support such assumptions were not available.

Because of its desirable properties, sulfuric acid retained its position as the most universally used mineral acid and the most produced and consumed inorganic chemical, by volume. Data based on USGS surveys of sulfur and sulfuric acid producers showed that reported U.S. consumption of sulfur in sulfuric acid (100% basis) decreased slightly. Reported consumption figures do not correlate with calculated apparent consumption owing to reporting errors and possible double counting in some data categories. These data are considered independently from apparent consumption as an indication of market shares rather than actual consumption totals.

Agriculture was the leading sulfur-consuming industry; consumption increased to 9.11 Mt compared with 8.51 Mt in 2003. Reported consumption of sulfur in the production of phosphatic fertilizers was 3.2% more than that of 2003, and reported consumption of sulfur used in other agricultural chemicals including sulfur fertilizers increased by 23.3%. According to export data from the U.S. Census Bureau (2005), the estimated quantity of sulfur needed to manufacture exported phosphatic fertilizers decreased slightly to 5.1 Mt.

The second ranked end use for sulfur was in petroleum refining and other petroleum and coal products. Producers of sulfur and sulfuric acid reported a 13.2% increase in the consumption of sulfur in that end use. Demand for sulfuric acid in copper ore leaching, which was the third ranked end use, increased by 7.4% as a result of increased copper production from leaching operations.

The U.S. Census Bureau (2005) also reported that 3.08 Mt of sulfuric acid was produced as a result of recycling spent and contaminated acid from petroleum alkylation and other processes. Two types of companies recycle this material—companies that produce acid for consumption in their own operations and also recycle their own spent acid and companies that provide acid regeneration services to sulfuric acid users. The petroleum refining industry was believed to be the leading source and consumer of recycled acid for use in its alkylation process.

Stocks

Yearend inventories held by recovered elemental sulfur producers decreased to 185,000 t, or about 10% less than that of 2003 (table 1). Based on apparent consumption of all forms of sulfur, combined yearend stocks amounted to about a 5-day supply in 2004, compared with a 6-day supply in 2003, a 6-day supply in 2002, an 8-day supply in 2001, and a 6-day supply in 2000. Final stocks in 2004 represented 3.3% of the quantity held in inventories at the end of 1976 when sulfur stocks peaked at 5.65 Mt; this was a 7.4-month supply at that time (Shelton, 1978, p. 1296).

Although markets were favorable throughout the year, U.S. producers and logistics companies on the Gulf of Mexico were planning for the possibility of excess supplies in the future. Most refineries face difficult choices when sulfur production exceeds demand and could be forced to curtail refining if no outlet for sulfur is available. In addition, increased international demand for sulfur has created new markets for exported sulfur. For this reason, several sulfur forming projects were progressing. CF Martin Sulphur, L.P., a sulfur logistics company, was considering the construction of a sulfur forming facility in Beaumont, TX (North America Sulphur Review, 2004f). Gulf Sulphur Services Ltd. (a joint venture between The Mosaic Co. and Savage Industries, Inc.) announced plans to build a sulfur priller and sulfur terminal at Mosaic's Faustina, LA, phosphate plant. The facility will have sulfur forming, handling, and storage capabilities (North American Sulphur Review, 2004a). Oil refiners on the Gulf of Mexico were considering the installation of sulfur forming equipment at or near a port to protect against oversupply problems that would limit operations at their refineries. Plans were to build tanks to store about 24,000 t of molten sulfur and the capacity to form approximately 4,000 metric tons per day (t/d) (North American Sulphur Review, 2004c). When completed, all these facilities were expected to be used when surplus sulfur supplies make it necessary to seek alternative markets. In that way, these producers would have the alternative to seek international customers when sulfur was in oversupply in the Gulf of Mexico region.

Prices

The contract prices for elemental sulfur at terminals in Tampa, FL, which are reported weekly in Green Markets, began the year at \$67.50 to \$70.50 per metric ton. In August, prices decreased to \$63.50 to \$66.50 per ton and remained there until November when they fell to \$61.50 to \$64.50 per ton and remained at that level through the remainder of the year.

Based on total shipments and value reported to the USGS, the average value of shipments for all elemental sulfur was estimated to be \$32.50 per ton, which was 13.2% higher than that of 2003 and nearly three times the average value in 2002. This dramatic increase was a result of a strong U.S. economy, increased production at domestic phosphate fertilizer operations that consumes large quantities of sulfur, and increased sulfur demand worldwide. Prices vary greatly on a regional basis, which caused the price discrepancies between Green Markets and USGS data. Tampa prices were usually the highest reported because of the large sulfur demand in the central Florida area. At the beginning of 2004, U.S. west coast prices were listed at \$15 to \$20 per ton, higher values than these producers have obtained for many years. Nearly all the sulfur produced in this region is processed at forming plants, incurring substantial costs to make solid sulfur in acceptable forms that can be shipped overseas. The majority of west coast sulfur was shipped overseas. From May through December, west coast prices remained between \$12 and \$17 per ton.

Foreign Trade

Exports of elemental sulfur from the United States, which included the U.S. Virgin Islands, as listed in table 7, were 13.0% higher in quantity than those of 2003 and 16.4% higher in value because the average unit value of U.S. export material increased to \$66.68 per ton. Exports from the west coast were 668,000 t, or 70.4% of total U.S. exports.

The United States continued to be a net importer of sulfur. Imports of elemental sulfur exceeded exports by almost 2 Mt. Recovered elemental sulfur from Canada and Mexico delivered to U.S. terminals and consumers in the liquid phase furnished about 89.6% of all U.S. sulfur import requirements. Total elemental sulfur imports were slightly lower in quantity, but higher prices resulted in the value being 8.8% higher than it was in 2003. Imports from Canada, mostly by rail, were 3.4% lower in quantity, and waterborne shipments from Mexico were slightly higher than those of 2003 (table 9). Imports from Venezuela were estimated to account for about 10.4% of all imported elemental sulfur.

In addition to elemental sulfur, the United States also had significant trade in sulfuric acid. Sulfuric acid exports were slightly lower than those of 2003 (table 8). Sulfuric acid imports were 11.8 times that of exports (tables 8, 10). Canada and Mexico were the sources of 89.0% of U.S. sulfuric acid imports, most of which were probably byproduct acid from smelters. Canadian and some Mexican shipments to the United States came by rail, and the remainder of imports came primarily by ship from Europe. The tonnage of sulfuric acid imports was 2.64 times that of 2003, and the value of imported sulfuric acid increased in proportion. Although still a minor portion of sulfur imports, additional imported sulfuric acid was required to meet the increased demand for sulfur in all forms. The most dramatic increase was in imports from Canada.

World Industry Structure

The global sulfur industry remained divided into two sectors—discretionary and nondiscretionary. In the discretionary sector, the mining of sulfur or pyrites is the sole objective; this voluntary production of native sulfur or pyrites is based on the orderly mining of discrete deposits with the objective of obtaining as nearly a complete recovery of the resource as economic conditions permit. In the nondiscretionary sector, sulfur or sulfuric acid is recovered as an involuntary byproduct—the quantity of output subject to demand for

the primary product irrespective of sulfur demand. Discretionary sources, once the primary sources of sulfur in all forms, represented 9.4% of the sulfur produced in all forms worldwide as listed in table 11.

Poland was the only country that produced more than 500,000 t of native sulfur by using either the Frasch or conventional mining methods (table 11). Small quantities of native sulfur were produced in Asia, Europe, and South America. The importance of pyrites to the world sulfur supply has significantly decreased; China and Finland were the only countries of the top producers with more than 500,000 t of sulfur produced whose primary sulfur source was from pyrites. About 78.3% of world pyrites production was in China, and 7.1% in Finland.

Of the 22 countries listed in table 11 that produced more than 500,000 t of sulfur, 15 obtained the majority of their production as recovered elemental sulfur. These 22 countries produced 90.2% of the total sulfur produced worldwide. The international sulfur trade was dominated, in descending order of quantity, by Canada, Russia, Saudi Arabia, the United Arab Emirates, Japan, and Iran; these countries exported more than 1 Mt of elemental sulfur each and accounted for 72.2% of total sulfur trade. Major sulfur importers, in descending order, were China, Morocco, the United States, India, Brazil, and Tunisia, all with imports of more than 1 Mt.

World production of sulfur was 3.5% higher in 2004 than it was in 2003; consumption was believed to be comparably higher also, making 2004 the 13th consecutive year that sulfur production exceeded consumption.

Prices in most of the world were believed to have averaged higher throughout the year than in the previous year, for the third consecutive year. Production of Frasch sulfur was slightly lower than that of 2003; production at the last mine in Poland remained about the same. Recovered elemental sulfur production was 3.8% higher, and byproduct sulfuric acid production increased slightly compared with those of 2003. Supplies of sulfur in all forms continued to exceed demand; worldwide sulfur inventories increased, much of which was stockpiled in Canada and Kazakhstan, although Canadian stocks actually declined owing to the strong international demand for sulfur. Globally, production of sulfur from pyrites was 5.9% higher.

Statistics compiled by the Oil & Gas Journal showed that the United States possessed 20.4% of the world's total refining capacity and 42.5% of the world's sulfur recovery capacity derived from oil refineries. The publication listed 674 oil refineries in 115 countries; only about one-half of these countries were reported to have sulfur recovery capacity (Stell, 2004[§]¹). Although the sulfur recovery data appeared to be incomplete, analysis of the data showed that most of the countries that reported no sulfur recovery at refineries were small and had developing economies and limited refining industries. In general, as refining economies improve in developing countries and the refining industries mature, additional efforts are made to reduce atmospheric emissions through installation of sulfur recovery units.

One of the few unregulated sources of manmade pollution is marine shipping. Marine pollution has thus far been left to shippers under the International Marine Organization's (IMO) Marine Pollution Treaty (MARPOL). An amendment to MARPOL that was ratified in October limited sulfur to 4.5% for ships in general operation beginning May 19, 2005. The allowable sulfur content of fuel burned in ships operating in the most crowded European waters [the North Sea, the English Channel, and the Baltic Sea, collectively known as the SOx emission control area (SECA)] was reduced to 1.5% effective May 19, 2006 (Fertilizer Week, 2004b).

The European environmental ministers' final proposal for the sulfur content in fuels for vessels sailing in European waters was a limit of 1.5% sulfur for all vessels in the SECA starting in 2007. The 1.5% limit applies to passenger vessels between ports within the European Union (EU) and the Baltic Sea beginning in May 2006 and the North Sea and the English Channel by 2007. Ships at berth in EU ports will be required to burn 0.1% sulfur fuel starting in January 2010 (Sulphur, 2004c).

Sulfur production in the Middle East is expected to increase to 7.5 Mt in 2012 from about 5.4 Mt in 2004. The expanded sulfur production can be attributed in large part to increased environmental awareness in the region, where it has become less acceptable to flare hydrogen sulfide instead of recovering sulfur. Most increased production will come from Iran, Qatar, Saudi Arabia, and the United Arab Emirates (Sulphur, 2004g).

World Review

Canada.—Canada was second only to the United States in production of byproduct sulfur and sulfur in all forms. It led the world in exports of elemental sulfur and stockpiled material. The majority of sulfur production came from natural gas plants in Alberta. For the second consecutive year, strong demand prompted remelting of stocks in Canada, resulting in a decrease of 1 Mt. At yearend, Canadian stocks were estimated to be about 13 Mt (North American Sulphur Review, 2005). Canadian offshore exports were 6.2 Mt, an increase of 17% compared with 2003, much of it going to China. Only one oil sands operation needed to stockpile sulfur, the bulk of Canadian production finding markets. Sulfur recovery at natural gas operations increased slightly, the first increase since 1998. Oil sands operations saw significant increases in sulfur recovery, with a combined 50% increase from three operations (North American Sulphur Review, 2004g).

Canadian production from natural gas has been declining for the past several years. A deposit discovered in 2004 could partially reverse that trend when it is tied in to existing processing plants in 2005. The estimated resource was reported to be 500 billion to 800 billion cubic feet of gas containing 35% hydrogen sulfide, the sulfur from which will be recovered at a rate of about 1,000 t/d (North American Sulphur Review, 2004b).

Alberta has huge deposits of oil sands with estimated reserves of 300 billion barrels of recoverable crude oil that contain 4% to 5% sulfur (Stevens, 1998). The crude oil resource in oil sands in Alberta is larger than the proven reserves of crude oil in Saudi Arabia. As traditional petroleum production in Canada declined, oil sands became a more important source of petroleum for the North American market. The proportion of Canadian production from oil sands was expected to increase to 21% in 2005 and 30% in 2010 from 9% in 2001 (Pok, 2002). Oil sands mines were being expanded by several companies. Because the bitumen recovered at the oil

¹ A reference that includes a section mark (§) is found in the Internet Reference Cited section.

sands deposits is high-density, high-sulfur petroleum, it must be upgraded to higher quality products or refineries must be adapted to process this type of raw material. Canadian upgraders and oil refineries were undergoing expansions and conversions to enable the processing of additional bitumen from expanded oil sands production. U.S. oil refiners were upgrading refineries in Colorado, Kentucky, Michigan, Minnesota, and Ohio to process synthetic crudes from Canada.

China.—China was the world's leading producer of pyrites with 56.3% of its sulfur in all forms coming from that source. The country also led in sulfur imports in 2004 with nearly 6.9 Mt (International Fertilizer Industry Association, 2005).

China's expanding industrialization has resulted in increased production of sulfuric acid, growing at an average rate of 8.2% per year from 1994 to 2003. In 2004, 38.7% of Chinese sulfuric acid production was from pyrites, 37.4% from elemental sulfur, 22.3% from smelter gases, and 1.6% from phosphogypsum. As in the United States, the major use for sulfuric acid was in the production of phosphate fertilizer. Sulfuric acid production was expected to reach 36 Mt in 2004, 38 Mt in 2005, and 42 Mt in 2010. Elemental sulfur and smelter gases are expected to become the more important raw materials for sulfuric acid production, and pyrites should become less dominant. Production of elemental sulfur is expected to increase as more is recovered at petroleum refineries (Sulphur, 2004g).

China's State Environmental Protection Administration (SEPA) drafted new vehicle emission standards equivalent to those enacted in Europe that were expected to be in force by 2008. Chinese motor fuels contain up to eight times more sulfur than gasoline in Europe and the United States. Vehicle emissions were the leading source of air pollution in China, having overtaken emissions from industry. The SEPA estimated that car exhaust would account for 79% of urban air pollution in 2005 (Sulphur, 2004a).

Because China has had serious air quality problems, especially in cities, the Government of China imposed a sulfur limit of 0.2% in diesel since 2000 to try to improve conditions. Beginning in 2001, 0.05% sulfur diesel was available in Beijing, Guangzhou, and Shanghai. Hong Kong requires even lower sulfur content in diesel used there. Additional sulfur recovery capacity will be required for China to expand the clean-fuel requirements to the entire country. Refiners must import more expensive, low-sulfur crude petroleum because the country lacks sulfur recovery capabilities (Vautrain, 2004).

Iraq.—One of the world's largest sulfur deposits is in northern Iraq where capacity was in place to produce 1 Mt per year of Frasch sulfur. Following Iraq's invasion of Kuwait in 1990, details on production at that mine were difficult to determine. It is believed that production continued at reduced levels until 2003, and stockpiles had accumulated. Scientists from the University of Maryland calculated that a fire at the Mishraq Mine sulfur stockpile, which was caused by sabotage in 2003, was the largest manmade release of sulfur dioxide ever recorded. The fire burned for almost 1 month and produced more sulfur dioxide than most volcanic eruptions. The fire released an estimated 600,000 t of sulfur dioxide, causing significant respiratory problems for the local population and \$40 million worth of damage to crops, although they expect no long-term environmental effects. Data was collected using instruments on two of the National Aeronautical and Space Administration's satellites (Sulphur, 2004e).

Kazakhstan.—The Tengiz oilfield and gasfield is the main source of current sulfur production in Kazakhstan. Located on the northeastern shore of the Caspian Sea in western Kazakhstan, Tengiz has been operated by Tengizchevroil (TCO) since 1993. The owners of TCO are ChevronTexaco (50%), ExxonMobil (25%), KazakhOil National Oil and Gas Co. (Kazakhstan's national oil and gas company) (20%), and LUKARCO (a joint venture between BP and Russian oil company LUKoil Oil Co.) (5%) (Chevron Corp., 2000). One of the world's large oilfields, Tengiz contains high-quality oil with 0.49% sulfur and associated natural gas that contains 12.5% hydrogen sulfide (Connell and others, 2000).

Production capacity at Tengiz was about 1.2 Mt in 2004, and it was expected to increase to 2.4 Mt in 2006. Stockpiled material, which was a source of contention between TCO and the Government of Kazakhstan in 2003, was estimated to be 8.5 Mt in 2004. Forming capacity that was installed to facilitate exports and minimize additional stockpiles totaled 800,000 t/yr for granulation and 400,000 t/yr for flaking. Granulation capacity was expected to increase to 1.6 Mt in 2006 (van Meurs, 2004, p. 3).

Sulfur also is recovered from the Karachaganak gas-condensate field in Kazakhstan near the Russian border. Because it is close to the Russian gas processing operation in Orenberg, sour gas from Karachaganak is treated at Orenberg. No gas treatment facilities have been installed at Karachaganak (Sulfur, 2001a).

Another large oilfield and gasfield was being developed in Kazakhstan by ExxonMobil (16.67%), Agip (16.67%), British Gas (16.67%), Shell (16.67%), ConocoPhillips (8.33%), and Inpex Corp. (8.33%). The consortium of companies agreed to the operating conditions for the giant Kashagan oilfield and gasfield under development in the Caspian Sea off Kazakhstan. Initial production was expected in 2008, and had the potential to make Kashagan one of the single largest resources of sulfur in the world. Actual production hinged on how much sulfur was reinjected (Sulphur, 2004d). Environmental groups objected to the implementation of acid gas reinjection at the field before extensive testing was completed that showed the technology presented no risk of contaminating the region with hydrogen sulfide and other sulfur compounds (Sulphur, 2004b).

Qatar.—Recovered sulfur production from natural gas processing in Qatar was estimated to be 360,000 t in 2004. Expansions of gas production in North Field are expected to result in dramatic increases of sulfur production starting in 2006 when sulfur production is expected to reach 735,000 t. Production potential increases were estimated to be 1.85 Mt in 2010 and 4.2 Mt in 2014. No stockpiling will be allowed. Because Qatar has only one deepwater port in the Arab Gulf and limited domestic demand for sulfur, reinjection of acid gases is being considered (van Meurs, 2004).

Russia.—Russia ranked second in the world in sulfur exporting with more than 4.3 Mt of elemental sulfur exports in 2004 (International Fertilizer Industry Association, 2005). The majority for Russia's sulfur production comes from natural gas at Gazprom's gas processing plants in Astrakhan and Orenburg, with an estimated 5 Mt of production in 2004.

Norilsk Nickel in Russia planned emission control improvements that would result in the recovery of 800,000 t/yr of sulfur from its smelters. The company planned to reduce sulfur dioxide emissions by 70% at its nickel smelter in north central Siberia by 2010 and recover elemental sulfur rather than the more common sulfuric acid from smelters. Pechanganickel aimed to reduce emissions at its nickel smelter near Murmansk by 90% (Sulphur, 2004f).

Venezuela.—Venezuela's Orinoco Basin is one of the world's major resources of crude oil. The crude petroleum found there is low-quality oil with sulfur content averaging about 4%, similar to the bitumen from Canadian oil sands operations. To make the material attractive for the open market, it had to be upgraded to higher quality synthetic crude with lower sulfur content before being shipped to foreign markets for further refining. Four operations processed Orinoco crudes at the Jose complex. They are Petrozuata [a joint venture between Conoco Inc. and Petróleos de Venezuela S.A. (PdVSA)], Sincor [an alliance of Total (47%), PdVSA (38%), and Statoil AS (15%)], the Cerro Negro project (a venture of ExxonMobil, PdVSA, and Veba Oel AG of Germany), and the Hamaca joint venture (owned by PdVSA, Chevron, and ConocoPhillips).

Completion of the Hamaca crude oil upgrading facility raised that operation's sulfur production capacity to 200,000 t/yr, bringing total capacity at the Jose industrial complex to 500,000 t/yr. Facilities there upgrade heavy crude petroleum to high-quality synthetic crude and, in the process, recover elemental sulfur, much of which is exported to the United States (Fertilizer Week, 2004a).

The Government of Venezuela increased the royalty on extra-heavy-oil-upgrading projects in Venezuela to 16.6% from 1%. Although the new rate is closer to a rate typical in the industry, the unexpected increase raised questions about future developments in that country and its commitment to honor agreements to encourage outside investments in domestic projects (North American Sulphur Review, 2004e).

Outlook

The sulfur industry continued on a path of increased production, slow growth in consumption, higher stocks, and expanded world trade. U.S. production from petroleum refineries is expected to increase substantially in the next few years as expansions, upgrades, and new facilities at existing refineries are completed, thus enabling refiners to increase throughput of crude oil and to process higher sulfur crudes. Production from natural gas operations was higher than it was in 2003, but significant decreases are expected from gas operations in Wyoming, the State in which about 70% of all U.S. natural gas sulfur is recovered. Of four large gas operations in the State, three expected decreases in production in 2004. Production at two decreased as a natural function of long-term extraction of natural gas. The operator of another gas plant was installing sour gas reinjection apparatus that would eliminate production at that site. The final company recently expanded its operation but was exploring the possibility of storing excess production underground. Theoretically, this material would be available to meet future needs. In reality, however, it represented an option for disposing of unwanted surplus material.

Worldwide recovered sulfur output is expected to continue to increase. The largest increases in recovered sulfur production through 2005 are expected to come from the Middle East's and Russia's growth in sulfur recovery from natural gas, Canada's expanded oil sands operations, and Asia's improved sulfur recovery at oil refineries. Refineries in developing countries should begin to improve environmental protection measures and in the future eventually approach the environmental standards of plants in Japan, North America, and Western Europe.

Experts from the natural gas industry estimated that the world demand for natural gas will grow by 2.5% per year during the next 20 years for a total 50% increase in demand. Producing 50% more gas means recovering at least an additional 50% in sulfur from that source. Future gas production, however, is likely to come from deeper, hotter, and more sour deposits that will result in even more excess sulfur production unless more efforts are made to develop new large-scale uses for sulfur. Other alternative technologies for reinjection and long-term storage to eliminate some of the excess sulfur supply will require further investigation to handle the quantity of surplus material anticipated (Hyne, 2000).

Byproduct sulfuric acid production will remain relatively steady in the United States so long as the copper smelters remain idle. With the copper industry's switch to lower cost production processes and producing regions, the four idle smelters may never reopen.

Worldwide, the outlook is different. Because copper production costs in some countries are lower than in the United States, acid production from those countries has not decreased as drastically, and increased production is likely. Environmental controls have been less of a concern in developing countries in the past. Many copper producers in developing and even in developed countries, however, are installing more efficient sulfuric acid plants to limit sulfur dioxide emissions at new and existing smelters. Planned and in-progress improvement projects could increase byproduct acid production significantly, although growth has been slower than previously expected.

Frasch sulfur and pyrites production, however, have little chance of significant long-term increases, although higher sulfur prices have resulted in the temporary increases in pyrites production and consumption. Because of the continued growth of elemental sulfur recovery for environmental reasons rather than demand, discretionary sulfur has become increasingly less important as demonstrated by the decline of the Frasch sulfur industry. The Frasch process has become the high-cost process for sulfur production. Pyrites, with significant direct production costs, is an even higher cost raw material for sulfuric acid production when the environmental aspects are considered. Discretionary sulfur output should show a steady decline. The decreases will be pronounced when large operations are closed outright for economic reasons, as was the case in 2000 and 2001. Sulfur and sulfuric acid will continue to be important in agricultural and industrial applications, although consumption will be less than production. World sulfur demand for fertilizer is forecast to increase by about 2.3% per year for the next 10 years; industrial demand is predicted to grow by 2.2% per year as a result of increased demand for copper and nickel leaching.

The most important changes in sulfur consumption will be in location. Phosphate fertilizer production, where most sulfur is consumed, is projected to increase by about 2.0% per year through 2011. With new and expanding phosphate fertilizer capacity in Australia, China, and India, sulfur demand will grow in these areas at the expense of some phosphate operations elsewhere, thus transferring sulfur demand rather than creating new demand. The effects were already being felt by the U.S. phosphate industry as reflected in the permanent closure of some facilities and reduced production at others. U.S. phosphate products supply domestic requirements, but a large portion of U.S. production is exported. Brazil, China, and India are primary markets for U.S. phosphatic

fertilizers. As the phosphate fertilizer industries develop in these countries, some of the markets for U.S. material could be lost. Sulfur will be required for phosphate production at new operations, and more sulfur producers will be competing for those markets.

Use of sulfur directly or in compounds as fertilizer is expected to increase, but this use will be dependent on agricultural economies and increased acceptance of the need for sulfur in plant nutrition. If widespread use of plant nutrient sulfur is adopted, then sulfur consumption in that application could be significant; thus far, however, growth has been slow.

Industrial sulfur consumption has more prospects for growth than in recent years, but still not enough to consume all projected surplus production. Conversion to or increases in copper leaching by producers that require significantly more sulfuric acid for the leaching operations than was used in 2003 bode well for the sulfur industry. Nickel pressure acid leach operations were using increased quantities of sulfur. Changes in the preferred methods for producing oxygenated gasoline, especially in Canada and the United States, might result in additional alkylation capacity that would require additional sulfuric acid. Other industrial uses show less potential for expansion. Production is expected to surpass demand well into the future.

Unless less traditional uses for elemental sulfur increase significantly, the oversupply situation will result in tremendous stockpiles accumulating around the world. In the 1970s and 1980s, research was conducted that showed the effectiveness of sulfur in several construction uses that held the promise of consuming huge quantities of sulfur in sulfur-extended asphalt and sulfur concretes. In many instances, these materials were found to be superior to the more conventional products, but their use so far has been very limited. Interest in these materials seemed to be increasing but only in additional research. When sulfur prices are high as they were in 2004, they are less attractive for unconventional applications where low-cost raw materials are the goal.

Regardless of the prevailing price increases in 2004 that signaled tight supplies, the worldwide oversupply situation is likely to continue. Unless measures are taken to use more sulfur, either voluntarily or through government mandate, large quantities of excess sulfur could be amassed in many more areas of the world, including the United States.

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TABLE 1
SALIENT SULFUR STATISTICS¹

(Thousand metric tons of sulfur content and thousand dollars unless otherwise specified)

	2000	2001	2002	2003	2004
United States:					
Quantity:					
Production:					
Frasch	900 ^e	--	--	--	--
Recovered ²	8,590	8,490	8,500	8,920	9,380
Other	1,030	982	772	683	739
Total ^c	10,500	9,470	9,270	9,600	10,100
Shipments:					
Frasch	W	--	--	--	--
Recovered ²	9,710 ³	8,470	8,490	8,910 ^r	9,410
Other	1,030	982	772	683	739
Total	10,700	9,450	9,260	9,600	10,100
Exports:					
Elemental ⁴	787 ^r	711 ^r	709 ^r	840 ^r	949
Sulfuric acid	62	69	48	67	67
Imports:					
Elemental	2,330	1,730	2,560	2,870 ^e	2,850 ^e
Sulfuric acid	463	462	346	297	784
Consumption, all forms ⁵	12,700	10,900	11,400	11,900 ^r	12,800
Stocks, December 31, producer, Frasch and recovered	208	232	181	206	185
Value:					
Shipments, free on board (f.o.b.) mine or plant:					
Frasch	W	--	--	--	--
Recovered ²	240,000 ³	84,700 ^e	100,000 ^e	256,000 ^e	306,000 ^e
Other	55,100	49,500	35,500	34,000	61,100
Total	295,000	134,000	136,000 ^r	290,000	367,000
Exports, elemental ⁶	57,400 ^r	52,000 ^r	43,100 ^r	54,400 ^r	63,300
Imports, elemental	39,400	22,100	26,800	70,600	76,800
Price, elemental, f.o.b. mine or plant dollars per metric ton	24.73	10.01 ^e	11.84 ^e	28.71 ^e	32.50 ^e
World, production, all forms (including pyrites)	59,300 ^r	59,500 ^r	60,600 ^r	61,900 ^r	64,100 ^e

^eEstimated. ^rRevised. W Withheld to avoid disclosing company proprietary data; included with "United States, value, recovered." -- Zero.

¹Data are rounded to no more than three significant digits except prices; may not add to totals shown.

²Includes U.S. Virgin Islands.

³Includes corresponding Frasch sulfur data.

⁴Includes exports from the U.S. Virgin Islands to foreign countries.

⁵Consumption is calculated as shipments minus exports plus imports.

⁶Includes value of exports from the U.S. Virgin Islands to foreign countries.

TABLE 2
RECOVERED SULFUR PRODUCED AND SHIPPED IN THE UNITED STATES, BY STATE¹

(Thousand metric tons and thousand dollars)

State	2003			2004		
	Production	Shipments		Production	Shipments	
		Quantity	Value ^c		Quantity	Value ^c
Alabama	234	231	7,710	228	228	7,560
California	1,070	1,060	20,600	1,050	1,050	20,500
Illinois	466	460	11,700	528	528	10,400
Louisiana	1,210	1,210	65,400	1,280	1,280	72,600
Michigan and Minnesota	39	39	195	35	38	1,040
Mississippi	534	548	19,700	495	501	19,800
New Mexico	42	42	(2)	34	34	(2)
Ohio	104	105	4,070	122	122	3,610
Texas	2,900	2,910	81,600	3,100	3,090	110,000
Washington	122	122	(2)	113	113	(2)
Wyoming	1,360	1,360	16,900	1,540	1,540	24,200
Other ³	834	837	28,100	849	886	36,300
Total	8,920	8,910	256,000	9,380	9,410	306,000

^cEstimated. ^rRevised.

¹Data are rounded to no more than three significant digits; may not add to totals shown.

²Some sulfur producers in this State incur expenses to make their products available to consumers.

³Includes Arkansas, Colorado, Delaware, Florida, Indiana, Kansas, Kentucky, Montana, New Jersey, North Dakota, Pennsylvania, Utah, Virginia, Wisconsin, and the U.S. Virgin Islands.

TABLE 3
RECOVERED SULFUR PRODUCED AND SHIPPED IN THE UNITED STATES,
BY PETROLEUM ADMINISTRATION FOR DEFENSE (PAD) DISTRICT¹

(Thousand metric tons)

District and source	2003		2004	
	Production	Shipments	Production	Shipments
PAD 1:				
Petroleum and coke	229	232	236	238
Natural gas	26	26	21	21
Total	255	258 ^r	256	259
PAD 2:				
Petroleum and coke	904	896	976	978
Natural gas	44	44	43	43
Total	948	940	1,020	1,020
PAD 3: ²				
Petroleum and coke	4,430	4,470	4,780	4,810
Natural gas	617	613	512	510
Total	5,050	5,080	5,300	5,320
PAD 4 and 5:				
Petroleum and coke	1,410	1,380	1,390	1,400
Natural gas	1,260	1,260	1,410	1,420
Total	2,670	2,640	2,800	2,810
Grand total:	8,920	8,910 ^r	9,380	9,410
Of which:				
Petroleum and coke	6,970	6,970	7,390	7,420
Natural gas	1,950	1,940	1,990	1,990

^rRevised.

¹Data are rounded to no more than three significant digits; may not add to totals shown.

²Includes the U.S. Virgin Islands.

TABLE 4
BYPRODUCT SULFURIC ACID PRODUCED IN THE UNITED STATES^{1,2}

(Thousand metric tons of sulfur content and thousand dollars)

Type of plant	2003	2004
Copper ³	590	600
Zinc ⁴	51	93
Lead and molybdenum ⁴	42	45
Total:		
Quantity	683	739
Value	34,000	61,100

¹May include acid produced from imported raw materials.

²Data are rounded to no more than three significant digits, may not add to totals shown.

³Excludes acid made from pyrites concentrates.

⁴Excludes acid made from native sulfur.

TABLE 5
CONSUMPTION OF SULFUR IN THE UNITED STATES^{1,2,3}

(Thousand metric tons)

	2003	2004
Elemental sulfur:		
Shipments ⁴	8,910 ¹	9,410
Exports	840 ¹	949
Imports ⁵	2,870	2,850
Total	10,900 ¹	11,300
Byproduct sulfuric acid:		
Shipments ⁴	683	739
Exports ⁵	67	67
Imports ⁵	297	784
Total	913	1,460
Grand total	11,900 ¹	12,800

¹Estimated. ²Revised.

¹Crude sulfur or sulfur content.

²Data are rounded to no more than three significant digits; may not add to totals shown.

³Consumption is calculated as shipments minus exports plus imports.

⁴Includes the U.S. Virgin Islands.

⁵May include sulfuric acid other than byproduct.

TABLE 6
SULFUR AND SULFURIC ACID SOLD OR USED IN THE UNITED STATES, BY END USE¹

(Thousand metric tons of sulfur content)

SIC ³	End use	Elemental sulfur ²		Sulfuric acid (sulfur equivalent)		Total	
		2003	2004	2003	2004	2003	2004
102	Copper ores	--	--	421	452	421	452
1094	Uranium and vanadium ores	--	--	4	2	4	2
10	Other ores	--	--	58	6	58	6
26, 261	Pulpmills and paper products	W	W	225	272	225	272
28, 285, 286, 2816	Inorganic pigments, paints, and allied products; industrial organic chemicals, other chemical products ⁴	5	W	71	154	76	154
281	Other inorganic chemicals	188	W	97	108	285	108
282, 2822	Synthetic rubber and other plastic materials and synthetics	--	--	82	70	82	70
2823	Cellulosic fibers including rayon	--	--	1	2	1	2
283	Drugs	--	--	2	1	2	1
284	Soaps and detergents	--	--	2	2	2	2
286	Industrial organic chemicals	--	--	22	25	22	25
2873	Nitrogenous fertilizers	--	--	206	209	206	209
2874	Phosphatic fertilizers	--	--	6,660	6,870	6,660	6,870
2879	Pesticides	--	--	11	16	11	16
287	Other agricultural chemicals	1,590	1,970	46	49	1,630	2,010
2892	Explosives	--	--	10	10	10	10
2899	Water-treating compounds	--	--	98	89	98	89
28	Other chemical products	--	--	45	105	45	105
29, 291	Petroleum refining and other petroleum and coal products	3,700	4,100	140	248	3,840	4,350
30	Rubber and miscellaneous plastic products	--	W	--	4	--	4
331	Steel pickling	--	--	58	9	58	9
333	Nonferrous metals	--	--	3	3	3	3
33	Other primary metals	--	--	9	6	9	6
3691	Storage batteries (acid)	--	--	13	29	13	29
	Exported sulfuric acid	--	--	1,420	26	1,420	26
	Total identified	5,480	6,070	9,700	8,770	15,200	14,800
	Unidentified	678	801	409	518	1,090	1,320
	Grand total	6,160	6,870	10,100	9,290	16,300	16,200

W Withheld to avoid disclosing company proprietary data; included with "Unidentified." -- Zero.

¹Data are rounded to no more than three significant digits; may not add to totals shown.

²Does not include elemental sulfur used for production of sulfuric acid.

³Standard industrial classification.

⁴No elemental sulfur was used in inorganic pigments, paints, and allied products.

TABLE 7
U.S. EXPORTS OF ELEMENTAL SULFUR, BY COUNTRY^{1,2}

(Thousand metric tons and thousand dollars)

Country	2003		2004	
	Quantity	Value	Quantity	Value
Argentina	(3)	25	12	604
Brazil	181 ^r	11,600 ^r	520	31,800
Canada	46 ^r	5,630 ^r	88	6,070
Chile	--	--	24	1,700
China	274 ^r	17,900 ^r	167	9,880
Colombia	4	380	19	1,380
Mexico	35 ^r	2,740 ^r	24	1,960
Morocco	236	9,230	35	1,740
Senegal	17	1,900	18	896
Switzerland	--	--	19	1,090
Other	47 ^r	4,890 ^r	23	6,170
Total	840 ^r	54,400 ^r	949	63,300

^rRevised. -- Zero.

¹Includes exports from the U.S. Virgin Islands.

²Data are rounded to no more than three significant digits; may not add to totals shown.

³Less than ½ unit.

Source: U.S. Census Bureau.

TABLE 8
U.S. EXPORTS OF SULFURIC ACID (100% H₂SO₄), BY COUNTRY¹

Country	2003		2004	
	Quantity (metric tons)	Value (thousands)	Quantity (metric tons)	Value (thousands)
Aruba	2,460	\$499	2,630	\$217
Canada	164,000	11,200	98,700	7,730
Chile	1	3	8,270	942
China	529	313	2,050	562
Dominican Republic	2,550	217	2,410	279
Ireland	506	795	3,490	1,530
Israel	1,120	336	236	349
Japan	135	312	67	118
Korea, Republic of	337	78	157	18
Mexico	4,030	471	44,100	2,190
Netherlands Antilles	11,200	689	10,200	484
Saudi Arabia	861	1,340	2,230	4,020
Singapore	185	56	52	55
Taiwan	547	461	595	454
Trinidad and Tobago	6,450	326	6,520	395
United Kingdom	282	231	142	24
Venezuela	2,700	211	16,800	849
Other	6,990 ^r	1,300 ^r	5,590	1,100
Total	205,000	18,900 ^r	204,000	21,300

^rRevised.

¹Data are rounded to no more than three significant digits; may not add to totals shown.

Source: U.S. Census Bureau.

TABLE 9
U.S. IMPORTS OF ELEMENTAL SULFUR, BY COUNTRY¹

(Thousand metric tons and thousand dollars)

Country	2003		2004	
	Quantity	Value ²	Quantity	Value ²
Canada	2,080 ^c	32,000	2,010 ^c	31,300
Mexico	534	26,500	545	28,200
Other	253 ^c	12,000	295 ^c	17,300
Total	2,870 ^c	70,600	2,850 ^c	76,800

^cEstimated.

¹Data are rounded to no more than three significant digits; may not add to totals shown.

²Declared customs valuation.

Source: U.S. Census Bureau and PentaSul North American Sulphur Service as adjusted by the U.S. Geological Survey.

TABLE 10
U.S. IMPORTS OF SULFURIC ACID (100% H₂SO₄), BY COUNTRY¹

Country	2003		2004	
	Quantity (metric tons)	Value ² (thousands)	Quantity (metric tons)	Value ² (thousands)
Canada	386,000	\$17,800	1,920,000	\$79,400
Germany	76,800	2,570	69,300	3,750
Mexico	167,000	2,450	217,000	5,670
Spain	62,400	3,140	--	--
Sweden	57,000	3,060	95,300	4,830
Other	159,000 ¹	10,300 ¹	98,500	10,600
Total	908,000	39,200	2,400,000	104,000

¹Revised. -- Zero.

¹Data are rounded to no more than three significant digits; may not add to totals shown.

²Declared cost, insurance, and freight paid by shipper valuation.

Source: U.S. Census Bureau.

TABLE 11
SULFUR: WORLD PRODUCTION IN ALL FORMS, BY COUNTRY AND SOURCE^{1,2}

(Thousand metric tons)

Country and source ³	2000	2001	2002	2003	2004 ^c
Australia, byproduct:^c					
Metallurgy	654	817	899	863	865
Petroleum	30	45	60	60	60
Total	684	862	959	923	925
Canada, byproduct:					
Metallurgy	831 ^r	762 ^r	703 ^r	614 ^r	621 ⁴
Natural gas, petroleum, tar sands	8,621	8,154 ^r	7,671 ^r	7,891 ^r	8,271 ⁴
Total	9,452 ^r	8,916 ^r	8,374 ^r	8,505 ^r	8,892 ⁴
Chile, byproduct, metallurgy^c	1,100	1,160	1,275 ⁴	1,430 ^r	1,510
China:^c					
Elemental	290	290	290	290	300
Pyrites	3,370	3,090	3,240	3,400	3,730
Byproduct, metallurgy	1,900	2,000	2,200	2,400	2,600
Total	5,560	5,380	5,730	6,090	6,630
Finland:^c					
Pyrites	260	270	359	341	336
Byproduct:					
Metallurgy	283	227	308	305	301
Petroleum	46	46	55	60	65
Total	589	543	722	706	702
France, byproduct:^c					
Natural gas and petroleum	887	837	787	816	765
Unspecified	260	260 ^r	229 ^r	196 ^r	196
Total	1,150 ^r	1,100	1,020 ^r	1,010 ^r	961
Germany, byproduct:					
Pyrites	30	61	--	--	--
Byproduct:					
Metallurgy	618	684	754	701 ^r	591
Natural gas and petroleum	1,753	1,749	1,745	1,661	1,560
Total	2,401	2,494	2,499	2,362 ^r	2,150
India:^c					
Pyrites	32	32	32	32	32
Byproduct:					
Metallurgy	359	458	458	539	539
Natural gas and petroleum	376	526	371	451	501
Total	767	1,020	861	1,020	1,070
Iran, byproduct:^c					
Metallurgy	50	50	50	50	60
Natural gas and petroleum	963	880	1,200	1,310	1,400
Total	1,010	930	1,250	1,360	1,460
Italy, byproduct:^c					
Metallurgy	203	203	142	127 ^r	113
Petroleum	490	540	560	565	575
Total	693 ⁴	743	702	692 ^r	688
Japan:					
Pyrites ^c	-- ^r	-- ^r	-- ^r	-- ^r	--
Byproduct:					
Metallurgy	1,384	1,319	1,326	1,281	1,263 ⁴
Petroleum	2,072	2,424	1,865	1,951 ^r	1,890
Total	3,456 ^r	3,743 ^r	3,191 ^r	3,232 ^r	3,150
Kazakhstan, byproduct:^c					
Metallurgy	300	310	260	325	325
Natural gas and petroleum	1,200	1,400	1,600	1,600	1,650
Total	1,500	1,710	1,860	1,930	1,980

See footnotes at end of table.